Development of Technique for Controlling the Nano-order Structure of Anodic Aluminum Oxide

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Abstract

In our developed surface treatment technology, we deposit multiple different layers by fine-structure surface treatment to maintain the cleanness level of each layer, increase the surface area, improve surface adhesion, and thus achieve longer run length. This time, we applied the principle of our surface treatment technology to the nano structure of anodic aluminum oxide. In the traditional anodic aluminum oxide, the micro-pores are too small to create a photosensitive layer inside the pores and so cannot contribute to surface adhesion. In this study, we resolved this problem by making a fine structure which has larger micro-pores at the top of the layers and smaller micro-pores at the bottom of the layers.

1. Introduction

The printing industry has been supporting the movement for reducing environmental burden by encouraging the introduction of eco-friendly printing systems, including the Green Printing certification system by the Japan Federation of Printing Industries.1) As a printing plate manufacturer, FUJIFILM has developed Computer to Plate (CTP) systems that produce only a small amount of industrial waste (developer waste) and Plate to Plate systems that recycle the aluminum of consumed CTP plates back to their raw materials.

Fig. 1 illustrates one of those environment-friendly systems. We have made efforts to reduce environmental burden in printing via various green activities throughout the life cycle of planographic products.

Among such efforts, we have provided ecological CTP systems, such as the liquid waste-free processless CTP system, Eco & Free System XZ-R, and the XP-series positive thermal CTP plates that can considerably reduce the amount of developer waste by using it in combination with the developer waste reduction system, XR-2000/5000.

In particular, by mounting the plate onto the printing equipment and realizing on-machine developing at the start of printing, we have created a completely processless CTP system with an ultimate environment-friendly design that does not require either alkaline developing or gum processing. Fig. 2 illustrates the stages of the processless CTP system. Different from alkaline developing CTP, neither alkaline developing nor gum processing is necessary; therefore, no associated processing equipment is required, either.2)

However, compared with alkaline developing CTP, that ultimate eco-oriented-design, processless CTP plate XZ-R needed further improvements in its printing durability. We therefore developed nano-order structure control technology using anodic aluminum oxide to resolve that problem and applied it to the support for the plate.
2. Characteristics of the support for our processless CTP plates

Fig. 3 illustrates the layer configuration of our processless CTP, XZ-R. The CTP consists of a stratified photosensitive layer, an anodic oxide film and an aluminum support with a relief (grained) structure. The properties required for the support are adhesion to the photosensitive layer for the imaging section and ink detachability, moisture retentivity, hydrophilicity and scratch resistance for the non-imaging section. To improve printing durability, which is of concern, it is necessary to enhance the adhesion of the support to the photosensitive layer without decreasing the functionality of the non-imaging section.

3. Design policy for the support of our CTP

3.1 Conventional technology

The Multi-Grain V (MGV), which is a support for conventional CTPs, has a relief structure consisting of the following three types of superimposed undulations: (i) large undulations with a wavelength in the order of tens of microns; (ii) medium undulations with a wavelength in the order of microns; and (iii) small undulations with a wavelength of submicron order. Fig. 4 shows the fracture surface structure of the conventional CTP support.

By using those multiple undulations with different wavelengths, it becomes possible to maintain and control the structure of each wavelength, which increases the flexibility of design and improves the balance of physical property values that have a trade-off relationship.

The physical property parameters that may affect the performance of the support are surface area, steepness, arithmetic roughness average (Ra) and density of locally deep parts (Dpn). The surface area has an influence on printing durability and the steepness, on contamination resistance and balance between water and ink. Ra affects printing wetness visibility and Dpn, sensitivity. Fig. 5 illustrates their significance.

(1) Large undulations
Enhancing the retention of dampening solution improves printing wetness visibility. The retention can be improved by increasing Ra. However, if it becomes too large, the unevenness of the photosensitive layer thickness increases, which has an impact on sensitivity. Reducing Dpn realizes an even dispersion of large undulations.

(2) Medium undulations
Medium undulations contribute to contamination resistance and balance between water and ink. Reducing their steepness prevents the retention of ink, which achieves a contamination-resistant support. However, at the same time, that decreases the surface area and affects the adhesion of the support to the photosensitive layer. Thus, printing durability decreases. That is, in optimization, there is a trade-off between contamination resistance and printing durability.

(3) Small undulations
Small undulations with a wavelength of submicron order do not affect contamination resistance. By superimposing those small undulations on medium ones with reduced steepness, low steepness and a larger surface area become compatible. That has achieved the cancellation of the trade-off between contamination resistance and printing durability.
3.2 New nano-order structure controlling technology

Conventional processless CTP uses an MGV support consisting of three sizes of undulations: large, medium and small. To improve the printing durability of our processless CTP by modifying the support design, we have developed a new technology to control the nano-order structure of the anodic oxide film. Specifically, we have improved an idea that has already been employed in the development of supports that have acquired a larger surface area and low steepness by superimposing short-wavelength undulations on longer-wavelength ones.

First, we considered forming a relief structure of undulations with a shorter wavelength than submicron order, applying conventional design principles of supports. To do so, we decided to use micropores, which are nano-order fine structures of the anodic oxide film originally intended to have scratch resistance. Fig. 6 illustrates the wavelengths of the conventional large, medium and small undulations and the micropore diameter of the anodic oxide film.

However, micropores at the surface layer of the anodic oxide film have small diameters between 5 and 10 nm and thus the photosensitive layer cannot conform to them. We then enlarged the micropores to make the layer to conform to them, but that resulted in a significant problem. That is, although the intended effect was achieved, the layer sank deep inside the micropores, which substantially decreased on-machine developability. Moreover, even if on-machine development was possible, the non-imaging section became prone to contamination during printing because ink got inside the enlarged micropores.

Fig. 7 provides conceptual images indicating the structural models of anodic oxide films: one having conventional micropores with a surface layer diameter between 5 and 10 nm; and the other having those with a surface layer diameter enlarged to over 10 nm.

To resolve that problem, we developed a technology to control the nano-order structure of the anodic oxide film and created one with a stratified structure consisting of larger-diameter pores (top layer) and small-diameter pores (bottom layer). Fig. 8 provides a conceptual image of a stratified anodic oxide film.

Near the surface, the photosensitive layer conforms to the inside of the larger-diameter pores, which enlarges the surface area of the film adhering to that layer. Thus, the film gains improved printing durability. On the other hand, in the bottom layer, the diameter of the pores is so small that the photosensitive layer and ink cannot infiltrate into the pores. That stratified structure improves printing durability without reducing developability or contamination resistance.

Furthermore, the structure does not change the forms of the large, medium and small undulations. Therefore, it is possible to increase the surface area while retaining the characteristics of the conventional support, in particular, steepness. Fig. 9 presents electron micrographs of the surface of a conventional support and the newly developed support. The latter images indicate that the larger-diameter pore layer was formed on the new support without changing the forms of any types of undulations.
Fig. 10 shows the relationship between the surface area and the steepness of the medium undulations that affects contamination resistance. It revealed that the new support can achieve a larger surface area than the conventional support with the same steepness.

3.3 Performance of processless CTP

The results of a performance evaluation with our developed processless CTP sensitive materials confirmed that they can increase printing durability while maintaining the essential performance properties of processless CTP: on-machine developability and contamination resistance (Table 1).

We have thus obtained a prospect for the industrial feasibility of this technology.

Table 1  Performance of new plate.

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<tr>
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<th>Newly developed support</th>
<th>MGV</th>
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</thead>
<tbody>
<tr>
<td>Exposure sensitivity</td>
<td>120mJ/cm²</td>
<td>120mJ/cm²</td>
</tr>
<tr>
<td>Printing durability (index)</td>
<td>150</td>
<td>100</td>
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<tr>
<td>On-machine developability</td>
<td>○</td>
<td>○</td>
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<tr>
<td>Contamination resistance</td>
<td>○</td>
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4. Conclusion

We developed a technology to control the nano-order structure of an anodic aluminum oxide film that is applicable to CTP supports. The technology enables:

• the creation of a stratified anodic oxide film with nano-order micropores consisting of a larger-diameter pore layer and a small-diameter pore layer;

• the improvement of printing durability by increasing the surface area of the top, larger-diameter pore layer of the film adhering to the photosensitive layer; and

• the retention of developability and contamination resistance by the lower, small-diameter pore layer preventing the photosensitive layer and ink from infiltrating into the bottom of the micropore layer.

Applying this technology to processless CTP substantially improves printing durability while retaining on-machine developability and contamination resistance.

We believe that, with this technology, we can contribute even more to the movement for environmental friendliness in the printing market.

References

