Development of Fujifilm Quality Thermal Photo Paper—a New Thermal Photo Printing Material

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Abstract

We developed a new thermal photo printing material. This new paper improves image quality, handling and reduces environmental impact during the production phase. This new paper utilizes a laminated base paper with the same high level of whiteness as silver halide photo print paper. The multi-layers, which contain a heat insulation layer, are coated on this base paper by using a production method based on FUJIFILM’s proprietary aqueous dispersion coating technology. Compared to previous thermal photo papers, this new paper achieves enhanced image quality (5% increase in whiteness; 20% increase in gloss). New production methods make it possible to increase the moisture content of the photo printing material itself, creating a surface resistance of approximately 1/1,000 of the conventional product, resulting in the improvement of antistatic property. This minimizes the tendency for freshly printed thermal photo prints to stick together, resulting in significantly increased handling ease. By adopting FUJIFILM’s proprietary aqueous dispersion coating technology that uses virtually no organic solvents, this new paper achieves a significant reduction in environmental impact during the production phase.

1. Introduction

With diversification of production methods for photo prints, a dye diffusion thermal transfer system (hereinafter referred to as D2T2 system) has been adopted in storefront instant printers, ID card-making machines, amusement printers, etc., owing to the simplicity and the high image quality. In the D2T2 system, the heat insulation of the receiving paper is an important property in utilizing the heat of the printer head for efficient dye transfer. We introduced a new heat insulation technology and enabled receiving paper production by water-based superimposition coating, which we have cultivated over the years. Further, by integration with a photographic support technology, we realized smooth tone reproducibility, high maximum density, excellent whiteness and high glossiness, and made it possible to provide prints of high image quality. In addition, we achieved an excellent effect also in print handleability. Here we report the contents.

Photo 1 Thermal paper and ink ribbon for D2T2 print system.

Photo 2 D2T2 Thermal photo print system “Princiao”.

2. Outline of D2T2 System

The principle of image formation by the D2T2 system is described briefly. The components are composed of an ink ribbon coated with a dye-containing ink layer, and a receiving paper having a receiving layer to receive the dye transferred from the ink ribbon. For image formation, the ink ribbon is brought into contact with the receiving paper, and then heated by a thermal head from the back side of the ink ribbon to thereby diffuse and transfer the dye from the ink layer to the receiving layer. The ink ribbon has a yellow ink layer, a magenta ink layer, a cyan ink layer and a surface protective layer formed on a thin PET support, and these are sequentially transferred to form a color image.
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Fig. 1 shows a configuration diagram of a printer. Between the thermal print head (TPH - this is referred to as thermal head in this report) and the platen roller facing thereto, the receiving paper and the ink ribbon are sandwiched with the receiving layer of the receiving paper kept in contact with the ink layer of the ink ribbon, and while these are scanned in the machine direction in that condition, a heat corresponding to an image information is given thereto by the thermal head to transfer the dye. After scanning three times for image formation with the yellow dye, the magenta dye and the cyan dye, and scanning one time for transfer for the surface protective layer, totaling scanning four times, image printing is finished.

Fig. 1 Composition of D2T2 print system.

Fig. 2 shows the characteristic curves of the new receiving paper which we developed this time. The horizontal axis indicates the applied energy amount, and the vertical axis indicates the visible density (corresponding to the transferred dye amount). 0.7 msec and 2 msec each mean the pulse period, indicating the characteristic curve corresponding to a high-temperature high-speed printer and that corresponding to a low-temperature low-speed printer, respectively.

Fig. 2 Characteristic curves of the new materials.

3. Development of New Receiving Paper

A receiving paper receives the dye transferred from an ink ribbon and forms an image. Accordingly, the paper is required to have high transfer performance on which a large amount of dye can be transferred with a small quantity heat. For the transfer performance, the heat insulation for storing the quantity of heat supplied from the thermal head on and around the surface of the receiving paper and acceptability of efficiently receiving the dye diffused from the ink ribbon are important. Accordingly, the basic constitution of the receiving paper comprises a heat-insulating layer and a receiving layer formed on a substrate by coating. Regarding the constitution thereof, usual receiving paper generally comprises a heat-insulating layer of a heat-insulating void film (e.g., foamed polypropylene film) stuck to a substrate (e.g., coated paper) and a receiving layer formed thereon by applying a solution of a polymer having high dye acceptability dissolved in an organic solvent to it in a mode of coating.

In developing the new receiving paper this time, we developed our proprietary heat insulation technology and planned a new layer constitution. Further, we employed a water-based superimposition coating system for all the constitutive layers, for the first time in the world. Not substantially using an organic solvent, we succeeded in reducing the environmental load. In addition, we could take advantage of the high-accuracy superimposition coating technology which we had cultivated over the years in production of silver halide photo print materials.

The planning and introduction technology for receiving paper materials is described below.

3.1 Layer Constitution of New Receiving Paper

Usual receiving paper comprises a heat-insulating layer of a void film stuck to a coated paper, and a receiving layer formed thereon in a mode of solvent coating. In the new receiving paper we developed this time, a subbing layer, a heat-insulating layer and a receiving layer are formed on a paper substrate double-laminated with polyethylene, in a mode of water-based superimposition coating. Fig. 3 shows a cross-sectional view of the new receiving paper.

Fig. 3 Cross section of a new paper.

The functions of the constitutive layers are described below.
3.2 Receiving Layer

The receiving layer is a layer to receive the dye diffused from an ink ribbon and form an image. The layer is required to have high acceptability for dye, for which the receiving polymer is required to be supplied as an aqueous dispersion thereof since the receiving layer is formed of a water-based coating liquid.

For the materials satisfying these requirements, we searched vinyl chloride-type, acrylic, polyester-type or the like polymer dispersions, and found that vinyl chloride-type materials are favorable. Further, we selected vinyl chloride/acrylate copolymers with an acrylate added thereto for regulating the glass transition temperature (T_g) thereof.

Fig. 4 shows one example indicating the preference of vinyl chloride-type materials. From Fig. 4, it is known that the receiving polymers having a lower glass transition temperature could attain better transfer.

![Fig. 4 Influence of components and glass transition temperature of receiving layer for receiving amount of dye.](image)

The receiving layer is required to have another property of releasability. The property is that the layer is, after heated while kept in contact with an ink ribbon, easily releasable from the ink ribbon. When the receiving layer has a lower glass transition temperature, then the transfer density may be higher, but the releasability of the layer is poorer and the peeling force between the receiving paper and the ink ribbon is thereby larger. When the peeling force increases, then there occurs peeling vibration to cause noise, and there may occur image failure of sticking or banding (see Photo 3). Further, in worse cases, there may occur blocking whereby the ink layer may undergo cohesion failure and may be transferred onto the receiving layer.

We searched release agents for satisfying both the enhancement of acceptability and enhancement of releasability, and found an effective fluorine-containing release agent, and introduced it into the receiving layer. Fig. 5 shows the effect of release agent addition. It is known that the force necessary for releasing the receiving paper from the ink ribbon after printing reduced depending on the added amount of the release agent.

![Photo 3 Example of sticking problem.](image)

3.3 Heat-Insulating Layer

The heat-insulating layer is a layer disposed for preventing the diffusion of heat from a thermal head and for promoting the dye transfer from the ink ribbon to the receiving paper, and this comprises mainly hollow polymer particles and a binder. For attaining high heat insulation, air having a low thermal conductivity is preferably used as the heat-insulating component. In usual receiving paper, air in the void film plays the role. In the new receiving paper, we employed hollow polymer particles containing air in polymer particles
The hollow polymer particles are dispersed in water, and enabled water-based coating. The hollow polymer particles contain water inside the particles while they are in dispersion, but in the drying step after coating, water evaporates to form a vapor phase.

As the binder, we employed gelatin for the purpose of imparting the necessary film strength, and for imparting good coatability.

Fig. 6 shows the results of comparison of high-power/low-power heat-insulating layers by simulation. This shows the situation how the heat applied to the back of the ink ribbon runs through the ink ribbon and diffuses into the receiving paper. The red line indicates the temperature profile in heat diffusion in the receiving layer having a high-power heat-insulating layer; and the black line indicates the temperature profile at 100°C and at 120°C in the receiving layer having a low-power heat-insulating layer. It is known that the high-power heat-insulating receiving paper undergoes little heat diffusion, and the ink ribbon and the receiving layer are kept at a high temperature in the area around the heating point.

Fig. 7 shows the relationship between the voidage of the heat-insulating layer and the transfer density. This means the increase in the dye transfer amount and therefore the increase in the density with the increase in the voidage, or that is, the air content.

3.4 Subbing Layer

In the dye diffusion thermal transfer system, a receiving paper is brought into contact with an ink ribbon, and the two are sandwiched between a thermal head and a platen roller and heated under pressure for printing on the paper. In this process, in order that the thermal head can be brought into uniform and stable contact with the material, it is desirable that the thermal head can suitably step in the contact part of the material. For this, the receiving paper is required to have cushionability. The new receiving paper is provided with a subbing layer comprising, as the main ingredient thereof, a flexible SBR having a low glass transition point, by which cushionability is given thereto.

3.5 Substrate

The new receiving paper comprises, as the substrate thereof, a double resin-coated paper (also referred to as WP paper) generally used in silver halide color paper. Accordingly, the new receiving paper is intended to have the same quality feel as that of silver halide color paper, though it is a dye diffusion thermal transfer paper. Simultaneously, the new receiving paper is intended to take advantage of the characteristics of whiteness, smoothness, electroconductivity (reduced chargeability) and the like for the performance of the paper.

In the new receiving paper, the hollow particles in the heat-insulating layer act as scattering bodies to exhibit whiteness, and in addition, the background color of the substrate is also reflected. Optimum planning of titanium dioxide, ultramarine (bluish pigment) and fluorescent brightener to be in the substrate brings about favorable whiteness that has.
high brightness and is not yellowish (see Table 1).

<table>
<thead>
<tr>
<th>Whiteness</th>
<th>FUJIFILM’s Usual Paper</th>
<th>New Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO Whiteness</td>
<td>87 %</td>
<td>92 %</td>
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</table>

Table 1 Whiteness Comparison Usual Paper and New One.

According to the paper-making technology and the polyethylene lamination technology which we cultivated in the field of silver halide color paper applications, the finished substrate is homogeneous and the substrate surface is smooth. Accordingly, the new receiving paper has excellent gloss that usual receiving paper comprising a coated paper substrate could not have (see Table 2).

<table>
<thead>
<tr>
<th>Gloss</th>
<th>FUJIFILM’s Usual Paper</th>
<th>New Paper</th>
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</thead>
<tbody>
<tr>
<td>45° Regular Reflection Light Received</td>
<td>73 %</td>
<td>92 %</td>
</tr>
</tbody>
</table>

Table 2 Gloss Comparison Usual Paper and New One.

An antistatic electroconductive layer is formed on the back of the substrate. Accordingly, the surface electric resistivity of the new paper is lowered to about 1/1,000 of that of usual paper, and the static chargeability thereof is greatly reduced. Since usual receiving paper is much statically charged, and therefore the prints are poorly slidable in aligning them after taken out of the collector part, and therefore improving the paper is required from the viewpoint of the operability thereof. The new receiving paper improved this.

Photo 5 shows the collection operation after continuous printing. Usual receiving papers (left photo) were much charged and were poorly slidable, and it was difficult to align them after collection. On the other hand, the new imaging papers (right photo) could be readily aligned, and their operability was greatly improved.

4. Conclusion

We newly developed a dye diffusion thermal transfer paper excellent in whiteness and gloss and improved in operability after collection owing to reduced chargeability. All the constitutive coating layers on the substrate are formed of water-based coating liquids substantially not using an organic solvent, and the environmental load in the process of producing the receiving paper was greatly reduced.

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