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Development of New Inkjet Ink for Leathers

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Abstract

In industrial printing, digital printing which can handle a large variety of substrates has been demanded. Digital printing employing inkjet system using UV ink has been adopted to print images on variations of substrates, but UV-ink contains Volatile organic compounds (VOC). Aqueous-ink is relatively VOC-less but can't handle a variety of substrates. We solved these problems by developing new aqueous resin ink. The aqueous resin ink has high durability on leathers and the compatibility to variations of substrates.

Introduction

Printing to leathers has been getting attention on digital printing. The single word "leather" covers a lot of types, natural leather which is tanned animal skins, synthetic leather which is made of synthetic resin such as polyurethane, polyvinyl chloride and nylon, artificial leather which is made of microfiber and has the structure close to that of natural leather, and recycled leather. Depending on the application, there are many finishing methods, surface shape, and surface composition of leather. Digital printing employing inkjet system using UV ink has been adopted to print images on leathers for car seats, but UV-ink contains volatile organic compounds (VOC) and involves concern about human health. Solvent dye ink has also adopted to print images on leather, but it is not good at lightfastness. Digital printing employing inkjet system using aqueous ink for leathers which has less VOC than UV ink and high durability doesn't exist and is demanded.

Leather

Natural leather

In a word, natural leather is a tanned animal raw hides and skins. Since long ago, raw hides and skins of various animals are tanned to leather. For example, bovine, pig, goat, sheep, house, deer, ostrich, snake, crocodile, and lizard. Each animal is classified into detailed categories according to age, gender, and size. Food and Agriculture Organization of the United Nations reported that the bovine leather which is made of bovine skins is a large portion of all leather production in the world [1]. This is because bovine is the most consumed animal in the world as meat for human consumption, and leather is made from raw hide as a by-product of the meat. There are a lot of the production process to change from raw hides and skins to leather. It is not too much to say that tanning is the most important process to give the leather various function which is heat resistant, softness, corrosion resistance, strength and so on. After the tanning process, the painting process adds color, glossy and high durability to leather through staining and fatliquoring (Figure 1).

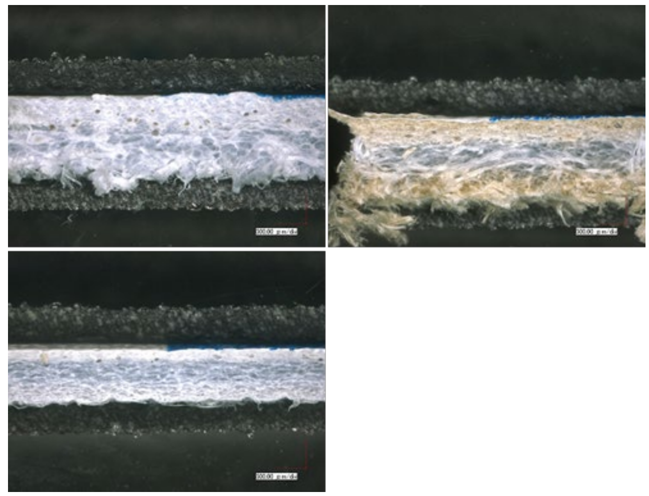

Figure 1. *Cross section of bovine (upper left; after staining and fatliquoring process, upper right; after painting process for color, lower left; after painting process for durability)*

Synthetic leather

Synthetic leather is the natural cloth which is coated with synthetic resin, for example, polyvinyl chloride (PVC) and polyurethane (PU). PVC-type generally has durability and stain-resistance. PU-type has elasticity, flexibility and breathability. Synthetic leather has a similar surface to that of natural leather, but the cross section of synthetic leather is markedly different. There is the fabric layer in the synthetic leather (Figure 2). In the case of adding high-durability to the synthetic leather, it has the painting process as well as natural leather.

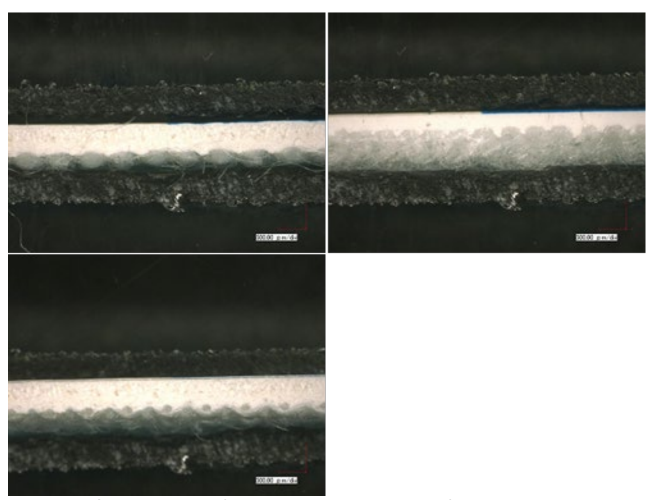

Figure 2. *Cross section of synthetic leather (upper left; without painting process, upper right; after painting process for durability, lower left; after painting process for durability and color)*

Compatibility of UV-ink and Dye-ink to leather

Printability

UV-ink (product A) and Dye-ink (product B) which have commonly been used for digital printing employing inkjet system on natural leather were printed image on seven leathers, including two natural leathers and five synthetic leathers. UV-ink was well printable for all leathers, but Dye-ink bleached against the synthetic leathers (Figure 3, lower right). UV-ink has printability for a wide range of leather from natural leather to synthetic leather.

Figure 3. *Image formed on leather (upper left; UV ink (product A) on the natural leather, upper right; Dye ink (product B) on the natural leather, lower left; UV ink on the synthetic leather, lower right; Dye-ink on the synthetic leather)*

Rubbing Resistance

To evaluate the rubbing resistance of UV-ink and Dye-ink on leather, Leather -Colour fastness tests- Test for colour fastness to rubbing - Part 2: Gakushin method (JIS K 6559-2:2017) was used. Gakushin (manufactured by INTEC) is an equipment used for the dyeing fastness test against rubbing of dyed textile and leather (Figure 4). After the leather was fixed to the stage, the test was carried out by making 100 reciprocations of a frictional part with a cloth and a weight of 200 g at a speed of 30 reciprocations per minute. Kanakin No.3, which is made of cotton was used as the cloth. Dry and wet rubbing were performed, and 95% to 100% water was added to the cloth for wet rubbing.

Figure 4. *Illustration of Gakushin (manufactured by INTEC)*

The grade corresponding value N was given by the following equation (1). Dx is the OD difference between the cloths before and after the test and the base of the logarithm is 10. The contamination grades were determined by using the conversion table from the class correspondence value N to the contamination grade. Rank 5 is the least transfer to the cloth, and 4 or more is preferable.

$$N = 5.5 - 1\mathrm{og}\,(Dx/0.18415+1)/1\mathrm{og}\,(2) \quad (1)$$

Table 1. Conversion table from the grade corresponding value N to the contamination grade

Grade corresponding value N	Contamination grade
4.5 ≤ N ≤ 5.5	5
3.5 ≤ N < 4.5	4
2.5 ≤ N < 3.5	3
1.5 ≤ N < 2.5	2
N < 1.5	1

The dyeing fastness of UV ink and Dye ink to the seven leathers are shown in Table 2. UV ink was a contamination grade of 4 or higher for both dry and wet rubbing to one natural leather and five synthetic leathers. For natural leather 1, the contamination grade of wet rubbing was 3. The dye ink was a contamination grade of 4 or higher for both dry and wet rubbing to the two natural leathers.

Table 2. Contamination grade of UV ink and Dye ink to leather

Leather	UV ink	Dye ink
Natural Leather 1	Dry; 5 Wet; 3	Dry; 5 Wet; 3
Natural Leather 2	Dry; 5 Wet; 5	Dry; 5 Wet; 3
Synthetic Leather 1	Dry; 4 Wet; 5	-
Synthetic Leather 2	Dry; 4 Wet; 5	-
Synthetic Leather 3	Dry; 4 Wet; 5	-
Synthetic Leather 4	Dry; 5 Wet; 5	-
Synthetic Leather 5	Dry; 5 Wet; 5	-

Aqueous Resin-ink Technologies

Problems to be Solved for Compatibility to the Leather

Aqueous pigment ink (product C) was printed on seven leathers as well as UV ink and Dye ink. For all leathers, abnormal images occurred (Figure 5). In printing image, ink droplets land before ink droplets that have already landed on a medium are not fixed and adjacent dots are combined. This brings about a phenomenon called beading coalescence (adjacent dots are combined). Beading coalescence is not preferable because it degrades the image quality, for example, shortage of embedding of image or horizontal streaks. The contamination grade was less than 4 for dry or wet rubbing to all leathers. In order to adapt aqueous ink to leather, beading coalescence and rubbing are problems to be solved. To solve two problems, we focused on an aqueous resin ink that can be printing image on non-permeating media and made an ink coating film with high strength.

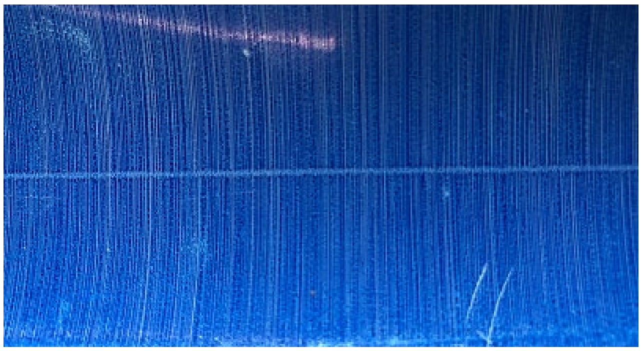

Figure 5. *Images formed with aqueous pigment ink (product C)*

Reduction of Beading Coalescence

To reduce beading coalescence, it is necessary that ink droplets are fixed on a medium by the time next ink droplets land thereon. Leather is generally painted coating material to add color and durability after the tanning process. When considering the reduction of beading, it is not possible to neglect the components of the coating material. Generally, acrylic resin and urethane resin are used for the coating of leather, and it is considered that compatibility between ink and coating layer is important. Analysis of the surface components of the seven leathers revealed that they were coated with urethane resin and/or acrylic resin. Ricoh reported that “Ricoh’s Aqueous Resin Ink” contained the solvents which had the ability of dissolving PMMA, which is the coating property of PVC media, to reduce beading coalescence on PVC media [2]. Therefore, the beading coalescence could be improved by adding a solvent that dissolves the coating layer of the leather, and the image formation on leather has been successfully achieved with an aqueous base ink (Figure 6). In addition, the contact angle with leathers also reduced by increasing the amount of solvent considered to dissolve the leather coating layer (Figure 7).

Figure 6. *Images formed with ink A (aqueous resin ink)*

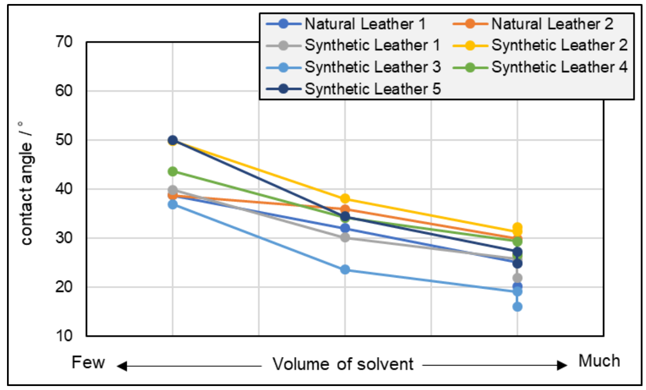

Figure 7. *Contact angle of aqueous resin ink to leather*

Improvement of Rubbing to Leather

To improve the rubbing to leathers, we attempted to use the urethane resin having the high Tg (glass-transition temperature), which has generally high durability. By containing urethane resin having the high Tg in aqueous resin ink, the rubbing to leathers was drastically improved, and the contamination grade to six leathers except natural leather 1 was 4 or higher. It is considered that not only the solvent in the ink dissolved the coating layer of the leather and the ink penetrated, but also the strong ink coating film was formed by the coating of the resin and the rubbing property became strong. However, the rubbing property is inferior to that of UV ink. For further improving the rubbing property which is equivalent quality to UV ink, we focused on the mechanical strength of the ink film. Coating film with high stress and low strain is hard and brittle. It is considered that the ink coating film with only large stress is insufficient for the leather. Leather is folded when processed into bags, wallets, etc. A hard and brittle ink coating film may crack the printed images during processing. Therefore, it is considered that an ink coating film having a large stress and a large strain is required. Dry/wet rubbing of three inks with different mechanical strength of ink film against seven leathers was evaluated (Figure 8). Ink B, which has a larger stress and strain than ink A, improved the contamination grade of wet rubbing to the two synthetic leathers from ink A. Ink C, which has a higher stress than ink B, improved the contamination grade of wet rubbing to one synthetic leather from ink B. Ink C had a contamination grade of 4, although the wet rubbing to one synthetic leather was inferior to UV ink. Dry/wet rubbing to the other six leathers was equivalent to or higher than that of UV ink.

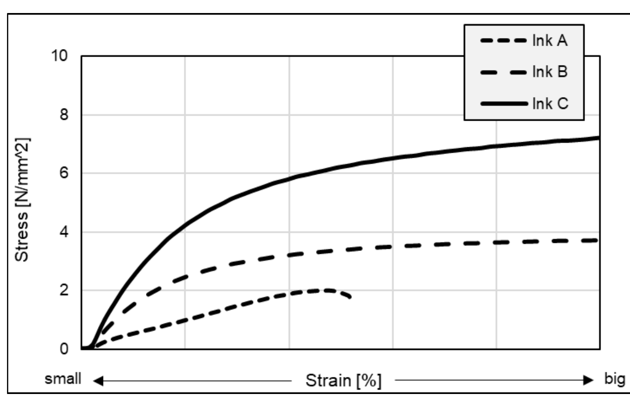

Figure 8. *Stress strain diagram of aqueous resin ink film*

Table 3. Contamination grade of aqueous resin ink to leather

Leather	Ink A	Ink B	Ink C
Natural Leather 1	Dry; 5 Wet; 3	Dry; 5 Wet; 3	Dry; 5 Wet; 3
Natural Leather 2	Dry; 5 Wet; 5	Dry; 5 Wet; 5	Dry; 5 Wet; 5
Synthetic Leather 1	Dry; 5 Wet; 5	Dry; 5 Wet; 5	Dry; 5 Wet; 5
Synthetic Leather 2	Dry; 5 Wet; 4	Dry; 5 Wet; 4	Dry; 5 Wet; 5
Synthetic Leather 3	Dry; 5 Wet; 4	Dry; 5 Wet; 4	Dry; 5 Wet; 4
Synthetic Leather 4	Dry; 5 Wet; 4	Dry; 5 Wet; 5	Dry; 5 Wet; 5
Synthetic Leather 5	Dry; 5 Wet; 4	Dry; 5 Wet; 5	Dry; 5 Wet; 5

Summary of New Inkjet Ink for Leathers

In order to improve the compatibility of the ink with the coating layer of the leathers, the composition of the coating layer of the leathers was analyzed and solvents which has the ability to dissolve the coating layer of leather was adopted. As a result, great images could be formed for both natural leather and synthetic leather. In addition, as the amount of the solvent was increased, the contact angle of the ink with respect to the leather became smaller.

It was also found that the mechanical strength of the aqueous resin ink film is important for image fastness on leather. By increasing the stress and strain of the ink film, the image fastness on the leather was improved until equal to or greater than the UV ink.

Conclusion

The newly developed ink is safe and environmentally friendly, and it can offer excellent image qualities on both natural leather and synthetic leather with high rubbing to leather equal to or better than UV ink.

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Author Biography

Naoto Shimura obtained his master degree in chemistry at the Sophia University in Japan in 2016. He entered Ricoh Co. Ltd. in 2016, and he specialized in inkjet ink formulation design