SPMC Technical Review

Development of Resin for Water-based Inkjet Ink for non-permeable media

SEIKO PMC CORPORATION
Resin Business Division Hiromasa Kataoka
Shigeki Nakata

1. Introduction

Unlike other printing methods such as offset printing, inkjet printing does not require printing plates, and its market is expanding in industrial applications to meet the need for a wide variety of printed materials in small lots.

Inkjet inks for industrial applications have been developed for non-permeable media such as films. Such inks include solvent-based inks that contain organic solvents as the main solvent and UV inks that contain polymerizable monomers as the main component. However, solvent-based ink has the problem of high environmental impact due to release large amounts of VOC. UV ink, on the other hand, cures immediately after printing, so VOC emissions are close to zero because VOC is either unused or trapped in the printed material, but there are issues of odor from the printed material[1] and toxicity of the initiator.

On the other hand, water-based ink, which contains water as its main solvent, has a low environmental impact and little effect on the human body, and the development of water-based inks that can be printed on non-permeable media has been considered of interest in recent years. However, water-based ink has a problem that its adhesion to non-permeable media is weaker than that of other types of ink.

Water-based ink contains water-soluble or water-dispersible resins in the ink, and when dried with heat after printing, those resins form a film on the media surface and fix to the media.

Resins are added to ink for various purposes. Among them, resins added for the purpose of providing coating film performance such as adhesion and coating film strength are called binders (bonding agents).

Water-based inks include resins as binder such as polyolefin, polyvinyl chloride, polyvinyl acetate, ethylene-vinyl acetate, acrylic resin and polyurethane.[2] However, since the adhesion of printed ink depends on the media material, it is required to choose the appropriate binder. When PVC or acrylic resin, which has relatively high polarity, is used as a binder, the adhesion to PVC and PET, which have high polarity, is good, but adhesion to OPP (biaxially oriented polypropylene), which has low polarity, is poor. On the other hand, when polyolefin is used as a binder, adhesion to OPP, which has a high affinity in terms of chemical structure, is good, but adhesion to PET is poor. Under these circumstances, there is a need for a binder for water-based inkjet ink with good adhesion to various base materials such as PVC, PET, and OPP.

2. Core-shell polymer emulsions

As mentioned above, various resins are used as binders for water-based inks. Among them, acrylic resins can be designed to meet the required functions and applications by combining various factors such as composition, molecular weight, and resin structure. We have accumulated knowledge of core-shell polymer emulsions containing acrylic or styrene acrylic resins as binders for water-based inks for gravure and flexographic printing. Core-shell polymer emulsions consist of the shell and core parts. A water-soluble

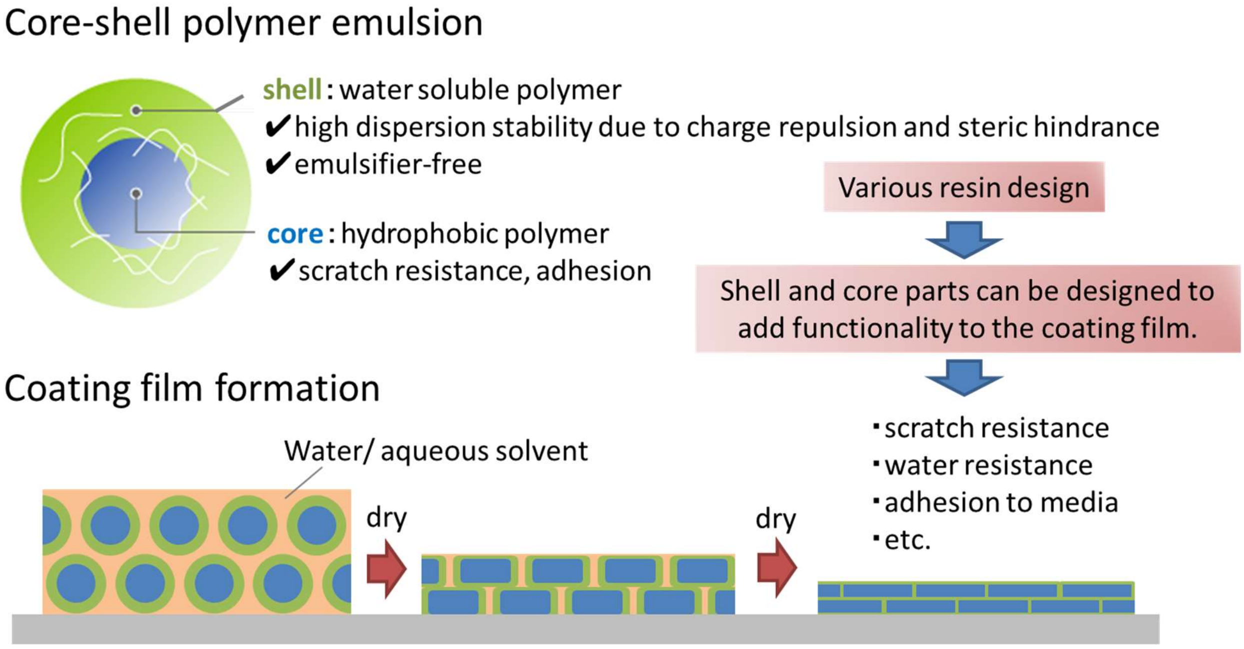

Figure 1. Core-shell polymer emulsions and coating film formation

polymer of the shell part with electric charge makes the emulsion has high dispersion stability due to charge repulsion and steric hindrance. Since emulsifiers are not contained, they have excellent water resistance, weather resistance, and mechanical stability. Furthermore, by designing the core and shell parts with different resin compositions to give a different function, the coating film obtained by drying the emulsion can have a variety of functions (Figure 1).

3. Cross-linking emulsions

One method to improve the coating film strength of printed materials is to cross-link the resin. Among various cross-linking designs, dehydration-condensation reaction of carbonyl-hydrazide is used for cross-linking, progressing at room temperature. The reaction of the polymer composed of diacetone acrylamide (DAAM) with adipic dihydrazide (ADH) is shown in Figure 2. Since DAAM has the carbonyl group capable of dehydration-condensation reactions and carbon-carbon unsaturated bond capable of addition polymerization, copolymerization of DAAM with other acrylic monomers can incorporate a cross-linking system into acrylic resin. Core-shell polymer emulsions containing acrylic resin incorporating this cross-linking system form a strong coating film as the cross-linking reaction proceeds during the drying process (Figure 3). On the other hand, in water, the cross-linking reaction does not proceed. Therefore, the emulsion is stable and suitable for a resin for inkjet inks, which require high storage stability. In this review, this emulsion is referred to as a cross-linking emulsion.

We have developed "HIROS^{TM}-X XJE-600", binder for water-based inkjet inks for non-permeable media, by designing an appropriate resin as a binder based on this cross-linking emulsion. Inkjet ink containing XJE-600 as binder has not only high film strength when printed, but also high adhesion to substrates with different polarity (PVC, PET, PP) and good ink storage stability.

Furthermore, by applying this technology and designing an appropriate resin as a primer, we developed HIROS^{TM}-X PR-007, a water-based primer for non-permeable media. The results of these study are presented in this review.

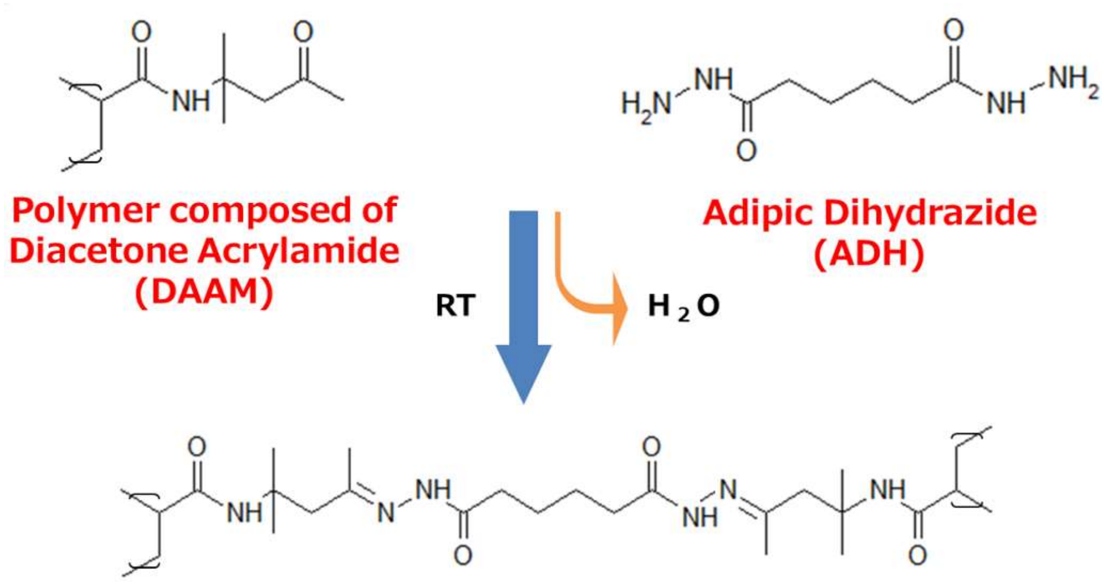

Figure 2. Reaction of polymer composed of diacetone acrylamide with adipic dihydrazide

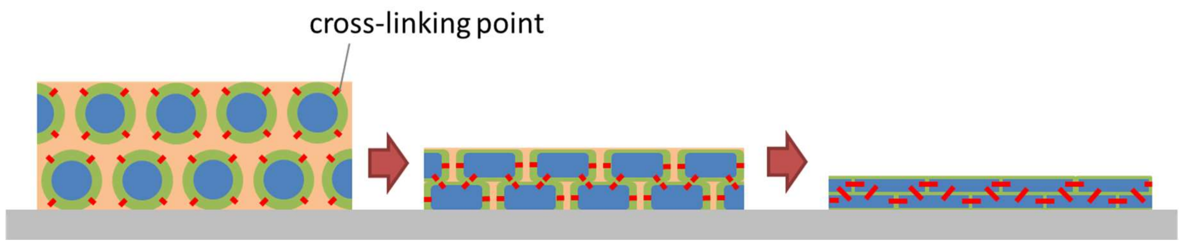

Figure 3. Coating film formation of cross-linking emulsions

4. “HIROS™-X XJE-600” Binder for Water-based Inkjet Ink for non-permeable media

We prepared inks containing XJE-600 (Table 1) as binder and its performance was evaluated. Water-based inkjet inks for evaluation were prepared by mixing pigment dispersion, XJE-600, organic solvents, surfactants, and ion-exchanged water. The resulting ink was filled into a water-based inkjet printer and printed in solid colors on commercially available PVC film (PVC), corona discharge treated PET film (PET), and corona discharge treated OPP film (PP), and the adhesion and various resistances of the resulting printed coating film were evaluated. The same evaluations were also conducted for inks using general-purpose acrylic emulsion A as reference binder. In addition, storage stability was evaluated for these inks. The results are shown in Tables 2 and 3. Both inks (1) and (2) showed good coating film resistance and ink storage stability, and ink (1) containing XJE-600 showed good adhesion to PVC, PET, and PP, while ink (2) containing acrylic emulsion A showed insufficient adhesion to PP. The photographs in Table 3 show the state of the coating film

Table 1. Typical physical properties of XJE-600

Name	XJE-600
Concentration [%]	43
Viscosity [mPa･s]	600
pH	8.7
Acid Value (theoretical value) [mgKOH/g]	30
Tg (theoretical value) [℃]	20
Ionicity	anion
Chemical composition	acrylic

Table 2. Evaluation results of inks

Ink	Binder	Adhesion			Durability		Storage stability
		PVC	PET	PP	Scratch resistance	Water resistance	
(1)	XJE-600	++	++	++	++	++	++
(2)	Acrylic Emulsion A	++	++	-	++	++	++

Coating film adhesion: Cellophane tape was applied to the coating film with a 1 mm width, 10 x 10 square cutout, and the evaluation was based on the number of squares that remained on the media when the tape was peeled off. (++: 90 or more, +: 80 to 89, -: less than 80)

Scratch resistance: Coating film on PVC was evaluated by the condition of the printed coating when it was subjected to 100 round trips on a cotton gauze under a load of 500g in a friction test for dyeing toughness. (++: The coating film did not peel off even after 90 round trips; +: The coating film began to peel off after 60 to 90 round trips; -: The coating film began to peel off after less than 60 round trips)

Water resistance: Evaluated in the same manner as the above scratch resistance evaluation, except that the cotton gauze was soaked into water.

Ink storage stability: The ink was stored at 60°C for 2 months and evaluated by the rate of change in viscosity before and after storage. (++: change of less than 10%, +: change of more than 10% to less than 15%, -: change of more than 15%)

after the cellophane tape was peeled off in the red framed area in Table 2. After peeling off with cellophane tape the coating film composed of XJE-600 did not peel off at all, whereas the coating film composed of acrylic emulsion A peeled off completely. These results indicate that XJE-600 has excellent coating film resistance and ink storage stability. And they also indicate that XJE-600 work as a binder for water-based inkjet inks that can be printed with high adhesion on non-permeable substrates with different polarity, such as PVC, PET, and PP.

Table 3. Cellophane tape peel test results of printed coating on PP

	Binder	
	XJE-600	Acrylic Emulsion A
After Peeling		

5. "HIROS^{TM}-X PR-007" water-based primer for non-permeable media

We have introduced a binder for water-based inkjet ink for non-permeable media, and we will also introduce a water-based primer developed by applying this technology. Primer is applied to substrates before printing ink, which is used to control ink blotting and improve substrate adhesion. As mentioned above, XJE-600 has excellent adhesion to various non-permeable media with different polarity, such as PVC, PET, and OPP. On the other hand, many general-purpose water-based inkjet inks do not adhere well to non-permeable media. We developed a water-based primer PR-007 based on XJE-600 technology.

When printing water-based inks on non-permeable media, the adhesion of the ink to the media can be enhanced by PR-007 coated before printing. One of the advantages of using PR-007 as a primer is that it is not necessary to consider substrate adhesion when designing inks. Here we introduce the results of printing various water-based inkjet inks on PVC, PET, and OPP coated with PR-007 (Table 4).

Table 4. Typical physical properties of PR-007

name	PR-007
Concentration [%]	27
Viscosity [mPa・s]	20
pH	8.5
Acid Value (theoretical value) [mgKOH/g]	52
Tg (theoretical value) [°C]	25
Ionicity	anion
Chemical composition	acrylic

PR-007 was applied as a primer to commercially available PVC film (PVC), corona discharge treated PET film (PET), and corona discharge treated OPP film (PP), and two general-purpose water-based inkjet inks with different binder resin types were printed on the primer. The adhesion was evaluated on the resulting printed coating film in the same method as described before. The same evaluation was also performed on coating films on various media without primer.

The evaluation results are shown in Table 5. It shows that in the system (1) in which PR-007 was used as a primer, the obtained coating film had good adhesion to the substrate regardless of the resin type of the topcoat ink. On the other hand, in the system without primer (2), adhesion to PET and PP was not sufficient.

Table 5. Adhesion evaluation results of printed coating film with primer

	Primer	Ink	Adhesion		
			PVC	PET	PP
(1)	PR-007	Acrylic resin	++	++	++
		Urethane	++	++	++
(2)	none	Acrylic resin	++	−	−
		Urethane	++	−	−

6. Conclusion

Ink containing XJE-600, a binder for water-based inkjet ink for non-permeable media, showed high film strength when printed, high adhesion to substrates with different polarity (PVC, PET, PP), and good ink storage stability. In addition, it was confirmed that water-based inkjet ink can be printed on various non-permeable media with high adhesion by using PR-007, a water-based primer for non-absorbent substrates. We will continue to study improvements for further performance enhancement in the future.

＜References＞

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Profile

SEIKO PMC CORPORATION
Resin Business Division
Akashi Laboratory

Hiromasa Kataoka

SEIKO PMC CORPORATION
Resin Business Division
Akashi Laboratory
Manager
Shigeki Nakata