Feature Article

Ink Jet Printing with Pigmented Inks for Photofinishing

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Ink jet printing technology is open to various applications because of advantages such as popularization of relatively cheap printers, litter free printing, ease of operation, easy maintenance, ability to print onto non-flat media, and ease of making prints of various sizes. However, some improvements are still needed in the application of photofinishing to replace color silver halide photographic prints. There are two kinds of ink jet printing systems in terms of inks: dye-based inks and pigmented ones. We know empirically that dye-based inks can produce better print quality than pigmented inks in many instances. Typical weak points of pigmented ink images are conspicuous grain, uneven low gloss, and bronzing. Pigmented ink images, however, generally show better image permanence than dye ink images. We have produced many ink jet prints with both kinds of inks and examined the characteristics of these images. Finally we focused our attention on the pigmented ink images. We determined the possibility of managing both image permanence and print quality, using microporous printing media with a specially coated layer for pigmented inks. We conclude that ink jet printing with pigmented inks can be applied for photofinishing purposes.

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Introduction

Image quality of ink jet printing has been upgraded through improvements in printers, printing media, and image-data processing techniques. Sometimes we can see an ink jet image of which print quality is very close to that of a silver halide color photograph. Ink jet printing technology is open to various applications because of the following advantages: popularization of relatively cheap printers, litter free when printing, ease of operation, easy maintenance, ability to print onto non-flat media, and ease of making prints of various sizes.

Inks are divided into two categories, dye-based inks and pigmented ones. As an experiential fact, we know that dye-based inks can produce better print quality than pigmented inks in many instances. Typical weak points of pigmented ink images are conspicuous grain, uneven low gloss, and sometimes a metallic shining appearance or bronzing. Pigmented ink images, however, generally show better image permanence than dye ink images. The difference in the image permanence between both kinds of images can be easily observed when they are exposed to ultraviolet light or oxidative gases such as ozone.

Both print quality and image permanence of ink jet images have to be upgraded from their present state for application to photofinishing in place of color silver halide photography. There are two routes to achieve this aim. The first uses dye-based inks with reinforcement after printing by covering the image with a film laminate, etc. Coating a resin layer on the printed surface is also useful for increasing the image permanence. However, these actions may introduce a new issue of increased costs.

Pigmented inks are used in the second route, which is the interest of this study. We will describe the characteristics of images printed with pigmented inks and suggest ways to improve image quality.

Experimental

An ink absorptive layer consists of silica particles, cationic polymers, and poly(vinyl alcohol).[1] We obtained silica particles from Nippon Aerosil Co. Ltd. Silica, cationic polymers, and poly(vinyl alcohol) were mixed in water with a rotary homogenizer for 5 minutes and then treated with a bead-mill of 2000 rpm at 15 – 25°C to get a good dispersed state. The pH of the dispersing solution was kept at 3 to 5 by adding 1N nitric acid. The degree of silica dispersion was evaluated by measuring average particle diameters and particle size distribution with Zetasizer 2000 (Malvern Co.).

A coating solution was prepared by adding water into the above dispersing solution to adjust its viscosity to 40 mPas•s at 40ºC and applied to resin coated paper as a substrate by a slide-bead coating method with a hopper. Thus an ink absorptive layer was made. Thickness of the ink absorptive layer was measured with a micrometer and average value of the thickness was evaluated from photomicrographs of cross sections. Volume of micro pores has been evaluated by measuring the volume of water which penetrates into the coated layer. The speed of ink absorption was measured with the Bristow method.[2]

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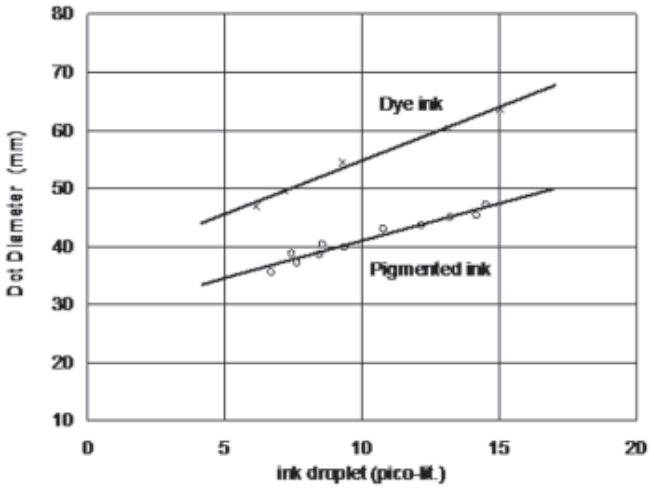

Figure 1. Relationship between image dot diameter and ink droplet volume.

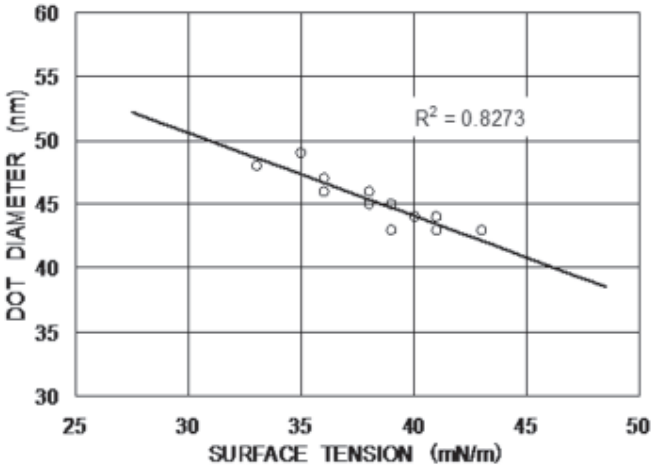

Figure 2. Relationship between dot diameter and surface tension of pigmented inks.

Surface gloss of the coated layer was measured according to JIS Z8741 or ISO 2813. We have also measured clarity according to JIS K7105 as one of the indices for evaluating print quality. Clarity is sometimes called distinctness of images which is abbreviated as DOI.

We used our trial printer with piezo type print heads to make various print samples. The print samples were irradiated with a 70000-lx Xe lamp at 23ºC and 60% RH for a prescribed time and the change in the color density and hue was measured to evaluate light-fastness of the printed images.

Color fading by oxidative gases has been discussed recently.[3–5] We have also examined the influence of ozone gas on printed images. We kept the print samples in a chamber with ozone gas of 6 ppm at 25ºC for 9 seconds and then measured color density and hue.

The resistance of print samples to water was evaluated through observation of blots after water soaking for an hour. We also observed the degree of abrasion when the print samples were rubbed with wet cotton swabs.

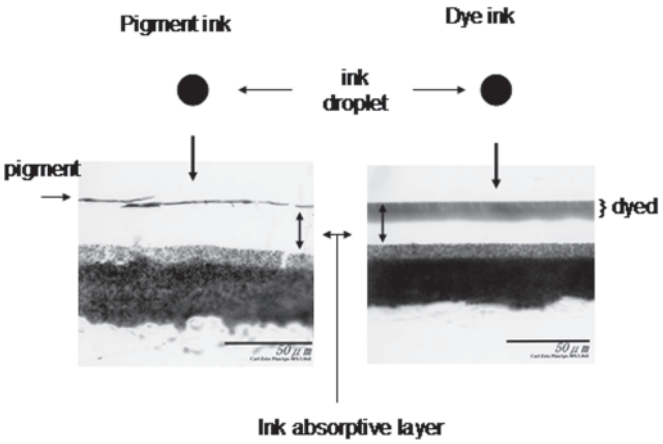

Figure 3. Photomicrographs of cross sections of printed area on microporous printing paper.

Results

Image Dot Size and Graininess

Figure 1 shows the relationship between image dot diameters and ink droplet volume. We can see in this figure that pigmented ink has made smaller dots than dye-based ink. This fact can be explained by considering that cohesive force operates among pigment particles and restrains ink droplets from spreading on a paper surface. The cohesive force was measured quantitatively in this study.

Close contact of image dots is needed to get high image quality. If the dots are placed positions far apart from each other, high optical density can not be obtained, and sometimes banding patterns show up according to print head movement. To avoid these unfavorable characteristics in printed images, we need to eject relatively large ink droplets and optimize printing conditions so the dots are in close contact. We thus may need print heads especially customized for pigmented inks.

It is well known that fluids of low surface tension spread easily. Although pigmented inks contain dispersed solids in the liquid and are not uniform solutions, the same phenomenon has been observed, as shown in Fig. 2. Consequently, we can control an image dot diameter to some extent by changing the surface tension of the pigmented ink.

The small dots of pigmented ink will create coarse impression in printed images and thus pigmented inks give frequently lower print quality than dye-based inks. This is a serious issue in the case of pigmented inks.

Gloss and Clarity

Figure 3 shows photomicrographs of the cross sections of printed areas of microporous printing paper. Pigment particles do not enter the ink absorptive layer but pile up on the surface. On the other hand, dye ink penetrates into the ink absorptive layer. The physical and optical properties of the surface printed with pigmented inks are determined by the state of aggregated pigment particles, while dye-based inks do not actually affect the surface state.

Piling of pigment particles determines the surface structure of printed regions of the image. The surface structure relates to surface smoothness, and smoothness dominates surface gloss. So the pigment will affect the surface gloss. Figure 4 shows that small particles give a smooth surface, and we can see the expected relationship between gloss and particle size in Fig. 5.

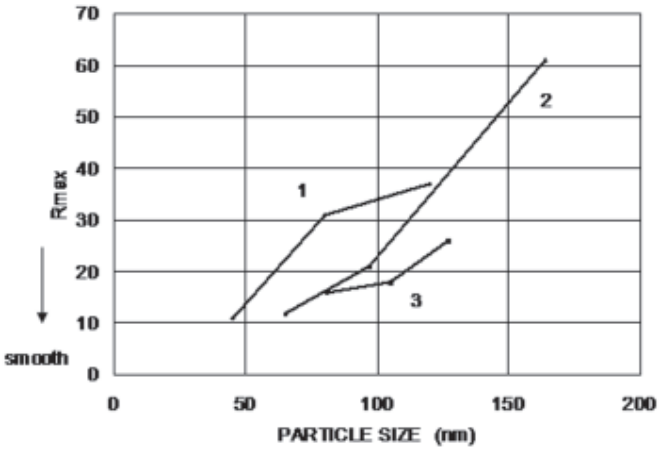

Figure 4. Relationship between pigment particle diameter and surface roughness. 1 - Pigment Yellow 74; 2 - Pigment Red 122; 3 - Pigment Blue 15:3.

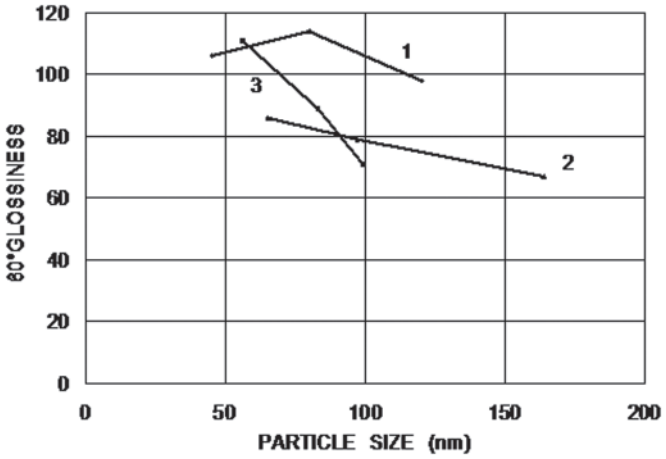

Figure 5. Relationship between surface gloss and pigment particle diameter. 1 - Pigment Yellow 74; 2 - Pigment Red 122; 3 - Pigment Blue 15:3.

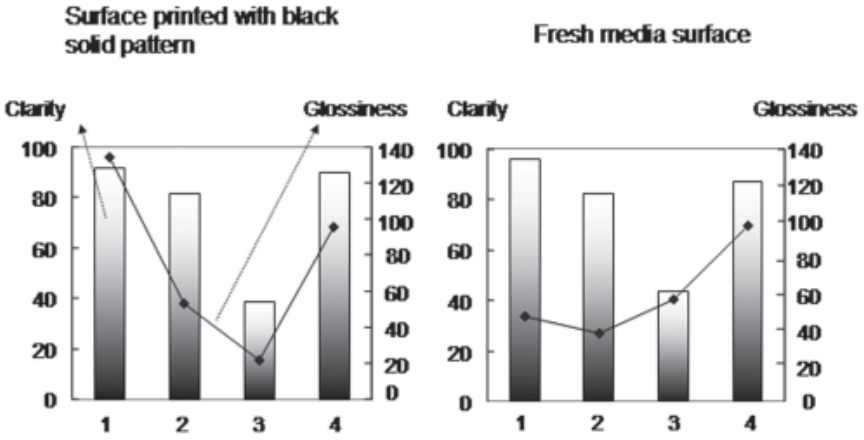

Figure 6. Clarity and 60-degree gloss of printing media surface. 1 - Glossy paper with a special layer and pigment ink; 2 - Glossy paper and dye ink; 3 - Satin surface paper and pigment ink; and 4 - Silver halide Photography

In order to make the surface printed with pigmented inks smooth, we needed certain reinforcement such as covering with a film laminate after printing.[6] To apply a thin polymer layer on the printed surface will also make the surface smooth. We have put a special layer on top of a silica microporous layer in the production of printing media and processed the overcoated layer especially after printing. This effort has resulted in a very smooth surface and we have observed high clarity as well as high gloss. The levels of these responses are similar to silver halide photographs as shown in Fig. 6.

Color Reproduction

Compared with dyes, many pigments have broader light absorption spectra in the visible region. Since broad light absorption generally causes the degradation of color reproduction because of color mixing, we may have the prejudice that pigmented ink images look dark and dull. In ink jet printing systems, however, we can choose a set of proper pigments in terms of color reproduction, and so the pigmented ink images are not always inferior to dye ink images in color reproduction as seen in Fig. 7. The lack of data in the green area in Fig. 7 resulted from the yellow color component. Another yellow pigment will be needed to upgrade color reproduction.

Image Permanence

It is well known that pigmented ink images are very stable to light exposure.[7] Figure 8 shows that the pigmented ink images are also stable when they are exposed to ozone gas whereas dye images are not so stable, especially on microporous media.[8]

Although the data are not shown in this article, changes in color and image blur were not observed at all when pigmented ink prints were soaked in water. On the other hand, blurring was observed with dye-based ink images. The difference in waterfastness is based on the colorants themselves, that is, pigment particles do not move on the printed surface, but dye molecules can easily migrate within the ink absorptive layers under the influence of water.

Figure 9 shows the resistance to wet abrasion. The state of printed surface was observed after being rubbed four times with wet cotton swabs, and we have made subjective evaluation. The evaluated values are plotted along the vertical axis. We expected that a portion of the pigment particles piled up on the media

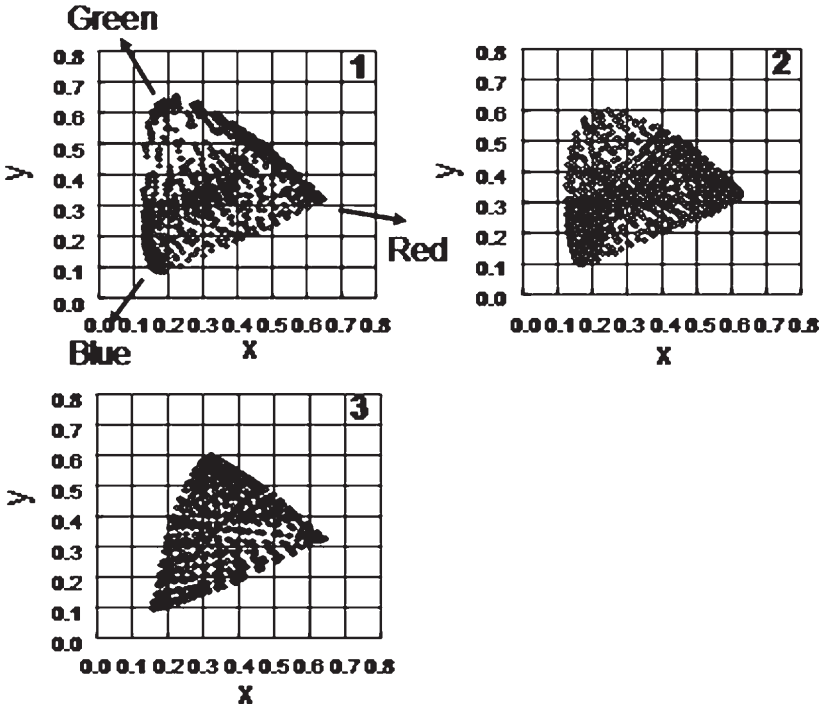

Figure 7. Color gamut. 1 - Pigmented inks + microporous media; 2 - Dye ink on microporous media; and 3 - Photographic paper with digital exposure.

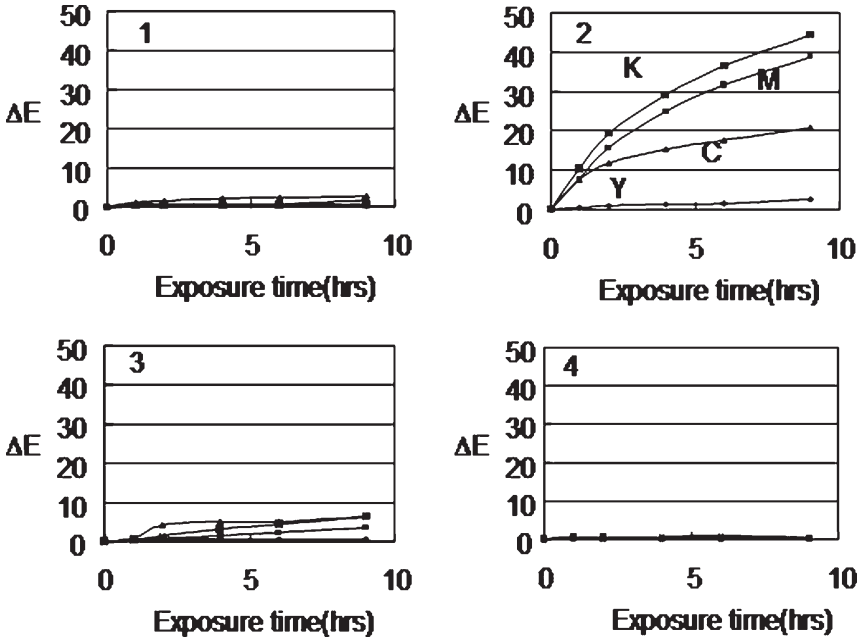

Figure 8. Ozone gas fading. Relationship between color shift (ΔE) and ozone exposure time. 1 - Pigmented ink on microporous media; 2 - Dye ink on microporous media; 3 - Dye ink on swellable media; and 4 - Silver halide photograph

surface could be removed by the swabs and the printed images would be damaged. Actually the response statistic for the pigmented ink images was relatively low as seen in Fig. 9. An abrasion resistant layer especially applied onto the microporous layer markedly raised the resistance to wet abrasion however. We also observed that the wet abrasion degrades dye images. As for the dye images on the microporous media, dye molecules move to the swabs and as a result the degradation of the images took place. In the case of swellable ink jet printing media, the ink absorptive layer itself was scraped away, leading to the destruction of the printed product. Photographic paper has a similar swellable layer. However, photographic layers are always intensely hardened using chemical agents, so that such destruction of the coated layers does not occur.

Discussion

Ink jet printing was considered originally to be primarily suitable for printing binary images. However, the innovations described below have recently made it pos-

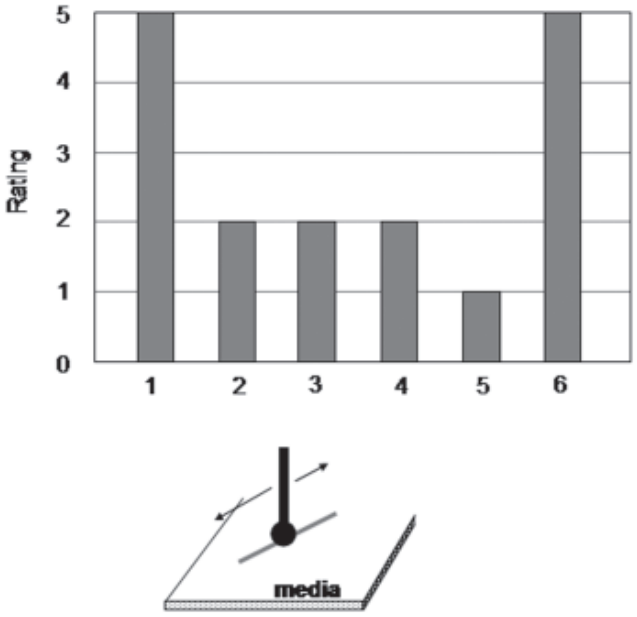

Figure 9. Resistance to wet abrasion; larger value of the response indicates greater abrasion resistance: 1 - Pigmented ink on microporous media with special layer; 2 - Dye ink on microporous media; 3 - Pigmented ink on micro-porous media; 4 - Pigmented ink on microporous media with satin surface; 5 - Dye ink on swellable media; and 6 - Silver halide photograph

sible to produce pictorial images with smooth tones and accurate color reproduction. The innovations are related to print heads capable of ejecting very small ink droplets, high-gloss printing media similar to photographic paper, and software for controlling printing conditions. Thus the application of ink jet printing systems has been extended as shown in Fig. 10.

In order to apply the ink jet printing technology to photofinishing, we have to consider various matters such as print quality, touch, applicability of post processing, productivity, maintenance, cost performance, and so on. Comparison of ink jet to silver halide photography is made in Table I in terms of photofinishing characteristics.

Figure 11 shows the conceptual relationship among dye-based ink jet, pigmented ink jet, and the target of photofinishing quality. In this article we have focused our discussion on route B of Fig. 11. Bronzing, coarse grain, non-uniform gloss, and low clarity (or DOI) are serious issues which must be addressed in order to upgrade print quality following route B.

As mentioned above, the diameter of an image dot printed with pigmented ink is generally smaller than obtained with dye-based ink (Fig. 1). The following efforts to enlarge the dot are needed for printing with pigmented inks in order to produce smooth images without a coarse grain impression: print-heads programmed for pigmented ink use only; inks of especially low surface tension (Fig. 2); and/or printing conditions for high density dot arrangement. These strategies are not so complicated as to prevent them from being applied in commercial printers today.

Gloss and clarity strongly affect perceived print quality. As shown in Fig. 3, pigment particles cannot enter the ink absorptive layers. Accordingly, the characteristics of the surface of printed area are determined by pigment particles rather than the ink absorptive layer itself. This fact means that the gloss and clarity of the printed area are essentially different from those of the non-printed area. This situation is peculiar to pigmented ink images and is not observed on dye ink images. According to our previous study,[9] the stability of printed images decreases with decreasing diameters of pigment particles. Consequently, we cannot reduce the size of pigment infinitely, even though the surface of image area becomes smoother with decreasing pigment particles as shown in Fig. 4.

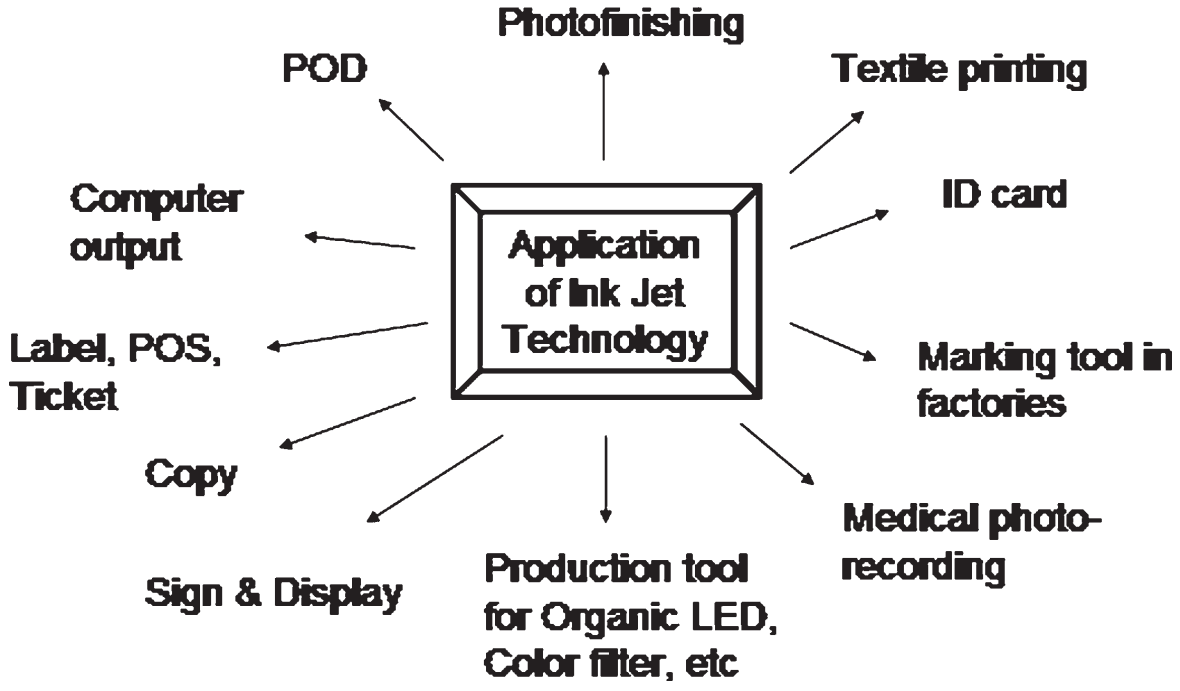

Figure 10. Applications of ink jet printing technology

TABLE I. Comparison of Ink Jet to Silver Halide Photography in Terms of Characteristics Required for Photofinishing

	Ink Jet (Dye ink)	Photograph
Features of Print Quality	clear color clear line image excellent whiteness repeatability of same quality	continuous tone smooth image without grain high optical density
Writeability	aqueous and oil-based pens can be used	oil-based pens can not be used
Productivity of Prints	capable of making large and various size prints easily relatively low print speed	restricted size adaptation high speed print
Maintenance	basically automatic machine check washing is unnecessary	check with a control strip by people every day need to wash dev. and fix. tanks
Supplies	paper and inks materials can be kept in ordinary office environment	"photographic paper or film, reagents for developing and fixing need to keep materials in a cool and dark room
Waste	inks	"developing and fixing solutions, waste water"
Cost	ca. twice as much as photograph	

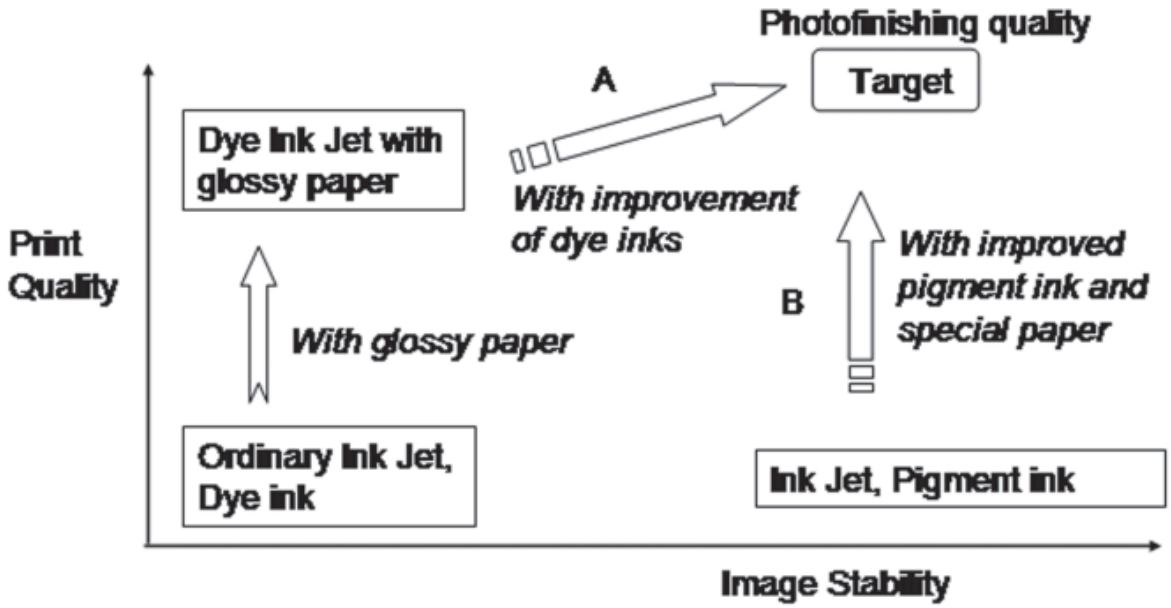

Figure 11. Conceptual relationship among dye-based ink jet, pigmented ink jet, and target of photofinishing quality.

The best method at present to solve the issue of gloss and clarity is to cover the printed images with a thin layer. We have tried to apply a specially coated layer on ink absorptive layers of silica microporous printing media. The layer was coated at the same time that the ink absorptive layers were coated. At the printing process, the media pass through rolls immediately after being printed. As shown in Fig. 6, both high gloss and high clarity were obtained. The results have been affected by the composition of the coated layer as well as the conditions of processing. The special layer has also improved the mechanical strength of printed images such as the resistance to scratching and resistance to wet abrasion (Fig. 9).

Conclusion

(1) We have studied the characteristics of images of ink jet printing with pigmented inks. Bronzing appearance, coarse grain impression, non-uniform gloss, and low clarity are the weak points of pigmented ink images. The possibilities for overcoming all these weaknesses has been discussed.
(2) We have shown that it is possibile to manage both image permanence and print quality by using microporous printing media with a specially over coated layer for pigmented inks.
(3) Based on the above facts, we conclude that ink jet printing with pigmented inks can be applied to photofinishing. ▲

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