The Durability of Digital Images on Photomedia

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Abstract

Digital images can now be produced by a number of different imaging technologies. Ink jet has emerged as the most popular method for printing digital photographs. This is a direct result of the developments in inks, printers, media, and software during recent years, providing high quality images which come close to those produced by silver halide technology.

One further challenge, for ink jet systems, is to match the image permanence of silver halide. Photographs produced by silver halide technology, generally have greater image stability and can be archived for many years, with little sign of any deterioration in image quality. The stability of ink jet images, in different environments, can however, be a problem. The influence of the environment on image stability will be considered.

Introduction

The challenge to the media, from the latest high-speed printers, is very demanding due to the increased rate of ink laydown. In recent years there has been a trend away from binder coated media towards microporous pigment coatings in order to provide instant drying of the printed image. The microporous media however, have other problems such as image stability, not observed for the gelatin based photomedia systems.

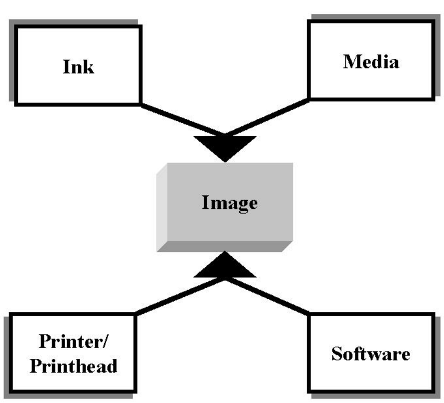

Figure 1. Factors which Influence the Formation of a Digital Image

A number of approaches have been used to solve the image stability issue. One solution is to use pigment colorants in the ink, however this can lead to other deficiencies. For dye-based chromophores considerable efforts have been made to improve the stability of these systems, particularly the magenta chromophore, which is often the most unstable to light.[1] There are also a number of approaches, which can be taken to modify the media to enhance image stability. The most successful approaches have involved the development of the ink and media systems in tandem (see Fig.1). This provides the optimum solution and developing the right combinations will be discussed in this paper.

Influence of the Ink on Image Stability

The most important ink components are the colorants and the ink vehicle. The different printers require different ink systems. The inks are carefully matched to the print heads for piezo and thermal printers. The current Xaar print heads use oil-based pigmentary inks. These require special coatings on the media (to absorb such inks). The majority of DOD (drop on demand) printers however, use aqueous inks, with a typical composition shown below (see Fig. 2)

Aqueous Ink {
- **Dye or Pigment**
- **Water**
- **Glycol**
- **Surfactant**

Figure 2. Typical Ink Components

The colorant can either be a water soluble dye (usually anionic) or a pigment.

Most of the dye-based colorants have been derived from the textile industry[2] although some have been developed from dyes used in the photo industry.[3,4,5]

An advantage for the anonic dye systems is that these can easily be fixed by the presence of a cationic charge within the media coating The cationic reagents however, can affect the image permanence.

Colorants/Pigments

Pigment chromophores, used in ink jet, have almost no stability issues. Commonly used pigments include:

Black:	Carbon black
Cyan:	β−Copper phthalocyanine
Magenta:	Dimethyl quinacridone
Yellow:	Azo pigment

Due to their complete insolubility and to the large number of molecules present in each pigment particle (typically 0.1 µm in size), these colorants are extremely stable to light and gas fading in all coating systems. They are also stable under different climatic conditons (temperature and humidities).

There are not many photomedia which are compatible with pigment-based inks. For photographic applications, specially matched media are required. Binder coatings do not tend to absorb pigment inks resulting in long drytimes and problems with smearing or smudging of the resulting image. When the media are designed and matched to the pigmentary ink systems, then photographic quality images, with up to 200 years of image stability, can result.

Dyes

Dye-based ink systems have problems with light stability, waterfastness, gas fading, humidity, and dark fading. Most of the properties relate to the structure of the chromophore, the solubility of the dyes and to the degree of aggregation present. The typical chromophores used for dye-based ink systems are listed below.

Black:	Disazo
Cyan:	β−Copper phthalocyanine
Magenta:	Azo-H acid, Azo-γ -acid, Xanthene
Yellow:	Azo

The coating composition also plays an important role in determining the image durability or permanence. There are possibilities for protecting the image and a great deal of research is currently being undertaken to solve the problem of dye permanence in ink jet photo applications.[6]

Influence of the Media on Image Durability

For high quality photopapers, the design of the coating has an important influence in determining the quality and stability of the image formed by an ink jet printer. Below are listed some of the properties of the receiver layers which can affect image stability.

(i) the chemistry of the coating
(ii) coat weight
(iii) pH
(iv) surface energy
(v) charge
(vi) crystallinity of the coating

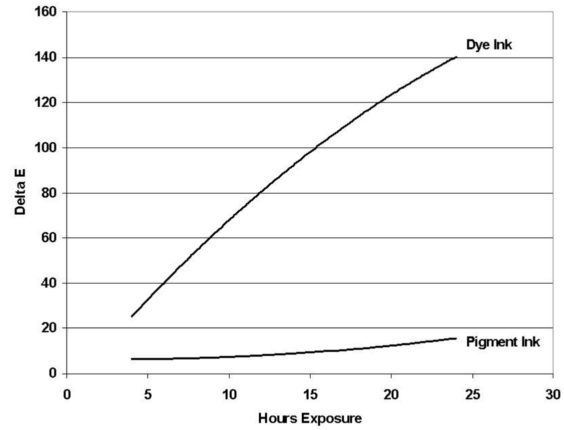

Figure 3. Lightfastness of Dye and Pigment Inks on a Microporous Photopaper

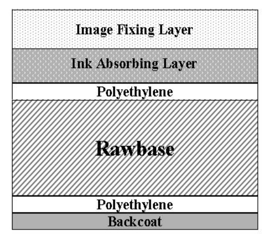

Figure 4. Resin Coated Photopaper

These and other factors all play a role in determining the permanence of the image produced by dye-based inks. The coating formulation is designed to produce an image by fixing the dyes in the upper layer (image fixing layer) and absorbing the ink vehicle into the bulk of the coating (ink absorbing layer). (See Fig. 4). The coating compositions have changed to accommodate the different requirements of the printer developments. The increased rate of ink laydown has led to the development of microporous receiver layers which can rapidly absorb the ink vehicles providing excellent image quality and instant drying.

Unfortunately the porosity, which exists in the ceramic receiver layers, has led to problems with image permanence. These problems are much less pronounced in standard binder rich media containing for example, gelatin, PVOH, PVP,etc.

Image Permanence in Different Media Types

The light fastness and ozone fastness of binder and microporous media types have been investigated.

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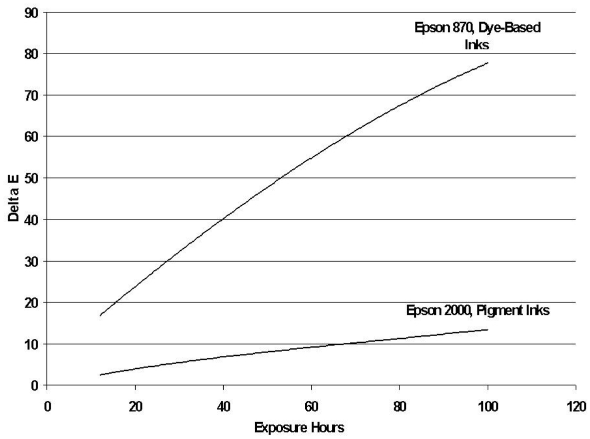

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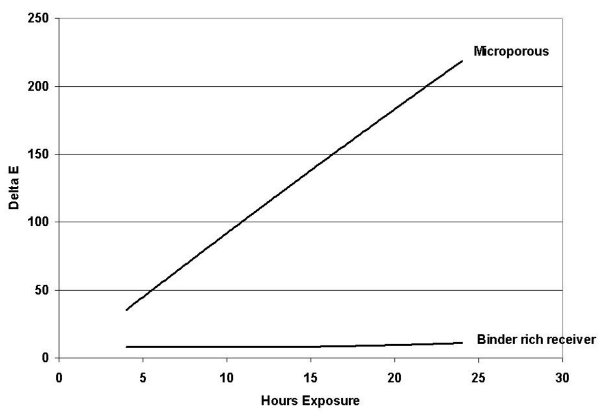

Figure 6. Ozone Fastness of Dye Based Inks on Different Photopaper Types

For photo media, consisting of mainly swellable polymer types, there is no real problem in terms of gas fading and the lightfastness is generally governed by the stability of the different chromophores. Most often the magenta dye is the most unstable to light fading. The fluorescent xanthene chromophore however, has poor image stability in most media types. The azo / hydrazo tautomerism, which exists for H-acid magentas, can lead to instability to light. The photographic azo -γ -acid chromophore is very stable to light but tends to be lower in Chroma compared with other magentas. On certain microporous media types however, the gamma acid magenta fades quite rapidly on exposure to light or ozone.

The ceramic systems, which absorb ink by a capillary mechanism have a high porosity built into the receiver layers. This results in a propensity to catalyze the destruction of chromophores by ozonolysis, O_3, present in the atmosphere.

This oxidative reaction rapidly destroys the cyan chromophore and indeed also destroys magenta and black. Only yellow appears to be more stable to this type of oxidative degradation.

AgX versus Ink Jet

In silver halide photography the image stability problems have been worked on for many years. Until the 1970's baryta papers (see Fig. 7 (ii)) where the baryta layer is the smoothing layer helping to provide gloss and whiteness) were popular and provided very stable black and white images.[7] An alternative is to put the coating layers directly onto rawbase/paper. These papers suffer from lower gloss and can have problems with cockle These papers are still used today for professional applications.

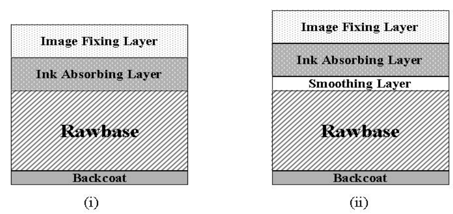

Figure 7. Paper glossy Photopapers

Resin coated papers mostly replaced the baryta papers and these now provide an alternative photo substrate (see Fig 4). The stability of the substrate has also been greatlyimproved since the first introduction of receiver layer papers. The polyethylene extruded substrate (see fig 4) is now the most widely used photographic substrate and this has also become the predominanat substrate for high end ink jet photographic papers[8]. This substrate has the look and feel of a AgX photograph. Silver halide has addressed the issue of image stability by improving the protection of the image formed within the gelatin emulsion layers.

The issues associated with gas fading, which have now become a significant problem in ink jet microporous systems, do not affect silver halide to the same extent due in part to the protection of the colorants by the gelatin medium. The pollutant gases O_3, NO_x etc., do not permeate through the gelatin layers and so the colorants are quite stable to this type of fading mechanism.

AgX has enhanced the light stability of the system by developing more stable colorants. These are mainly solvent soluble dye systems and so are less susceptible to fading mechanisms which require moisture. There are also many uv absorbers and light stabilisers present in the upper layers of the AgX media, which improve the light stability of the image.

Ink jet has mainly water soluble anionic colorants and so the presence of moisture within the layers can lead to instability of the image due to several different fading mechanisms.

Matching Ink and Media

For pigment–based inks there is no real interaction between the colorant and the media. The difficulty is to design a coating which readily absorbs the pigment ink without losing image quality. Problems for these include smudging, smearing of the image, and dull colours. Binder media cannot absorb the pigments into the coating and so the image remains on the surface and is easily damaged. By designing a porous surface structure for microporous media, the pigments can be absorbed into the photomedia producing high quality images with better stability than AgX. Some recent small format printers have indeed produced such ink/media matched systems for pigment-based systems. For dye-based inks there is a greater challenge and all the OEMs have developed ink and media sets matched to their high end printers to produce photographic quality prints. Some examples of such systems are illustrated in the graphs (see fig:8). In most cases the colorants all fade in light and ozone.

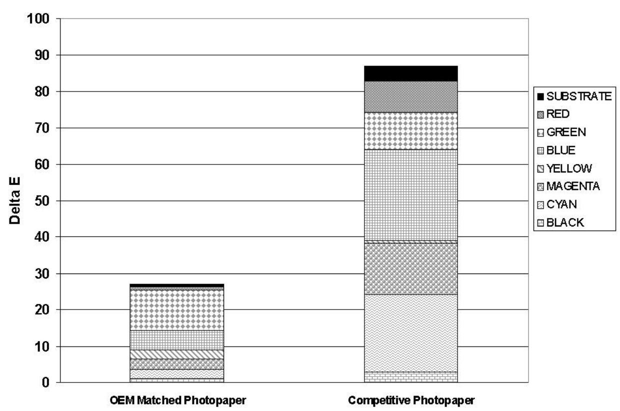

Figure 8. Ink/Media Matching for an OEM Printer

By matching ink and media to a photo-quality ink jet printer, the OEM's have achieved a higher level of performance. For the non-recommended media the challenge is to match this performance level. There is, nevertheless, still some way to go to achieve the permanence of AgX, using dye-based ink systems.

The ozone test was run for 24 hours at a concentration of 3.5ppm in ambient office conditons (approximately 23°C and 40% relative humidity). The standard lightfastness test was 50 hours with an irradiance of 1.2w/m^2 at 30°C and 60% relative humidity. This was using the Atlas 3000ci weatherometer and the ozone kit from Textile Innovators Corporation.

Conclusions

The performance level of the ink jet systems is getting closer to that tof the conventionla silver-based media In order to match the performance levels of AgX technology however, ink jet still needs to overcome many of the image stability issues. Pigment-based inks can achieve this and indeed provide an even greater level of stability than AgX prints. Dye-based inks however, which still dominate in most ink jet printers, do have a significant problem with image permanence in the different media types.

The challenge for the photomedia development in ink jet is to produce an instant drying receiver layer which also affords a high level of image permanence for dye-based chromophores. This can best be achieved by matching ink and media. The OEM's have already provided quality matched sets media for their photo-printers. The digital mini-labs will increase the ink/media combinations requirement which provide images close to that of AgX.

Pigments have no real issues with light fastness or ozone fastness on any of the different media types. It is not surprising that pigments are unaffected by the environment in which they are located due to their insolubility and lack of any interaction with the coating materials . However, pigment inks are not easy to formulate and there is a limited range of photopapers which are compatible with such ink systems.

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Biography

Aidan Lavery received his BSc and PhD in chemistry from Queen's University Belfast in 1980 and 1984. He spent two years at Edinburgh University carrying out postdoctoral studies on transition metal chemistry before taking up an academic position as a lecturer in chemistry for 3 years at Huddersfield University (1986-1988). In 1988 he joined ICI

/Zeneca where he spent 11 years being promoted to the position of Group Leader of the Physical Science team developing ink jet systems

In 1999 he took up his current position with Felix Schoeller Imaging as R&D director for Digital Imaging.

His interests have included the development of inkjet ink formations and the development of photomedia. He has considerable experience in ink/media interactions in ink jet. He has over 40 publications and 12 patents mainly on ink jet developments. Contact : alavery@felix-schoeller.com