

## CHAPTER 2

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Theoretical background

##### 2.1.1 Principle of inkjet printing<sup>3-5</sup>

Inkjet printing is a kind of non-impact printing, which a small liquid ink droplet is ejected under pressure through the print head nozzles onto a print substrate. The size of print head nozzle can vary from 10-100 micrometers depending on the technology. The technology of inkjet printing can be divided into two major types of inkjet printer as shown in Figure 2-1, drop-on-demand and continuous inkjet printer.

##### 2.1.1.1 Continuous inkjet printer

Continuous inkjet printer is the primary inkjet system formed by forcing ink under pressure (about  $3 \times 10^5$  Pa) out of one or more small nozzles. The working principle of this system is shown in Figure 2-2. A liquid jet tends to break up into a stream of droplets of a size and frequency determined mainly by the surface tension of the liquid, the pressure applied to it and the size of the nozzle. Applying a high-frequency alternating voltage (possibly up to 1 MHz) to a piezo-electric crystal in contact with the ink in the reservoir is a method to regularize a stream of uniformly sized and spaced droplets. The ink droplets are moved towards at a speed of 5-35 m/s. The ink stream undergoes a charged/no charged condition by binary switching. Individual ink droplets pass through a high voltage field of approximately 2000 V. The ink droplets become charged by induction and each droplet carries a charge

depending upon the voltage applied to the electrode. When the charged ink droplets pass through the high voltage field, they are repelled by the 2000 V electrode and are deflected into a reservoir. For the uncharged ink droplets, they pass through the high voltage field and are deposited onto the substrate to form part of an image.

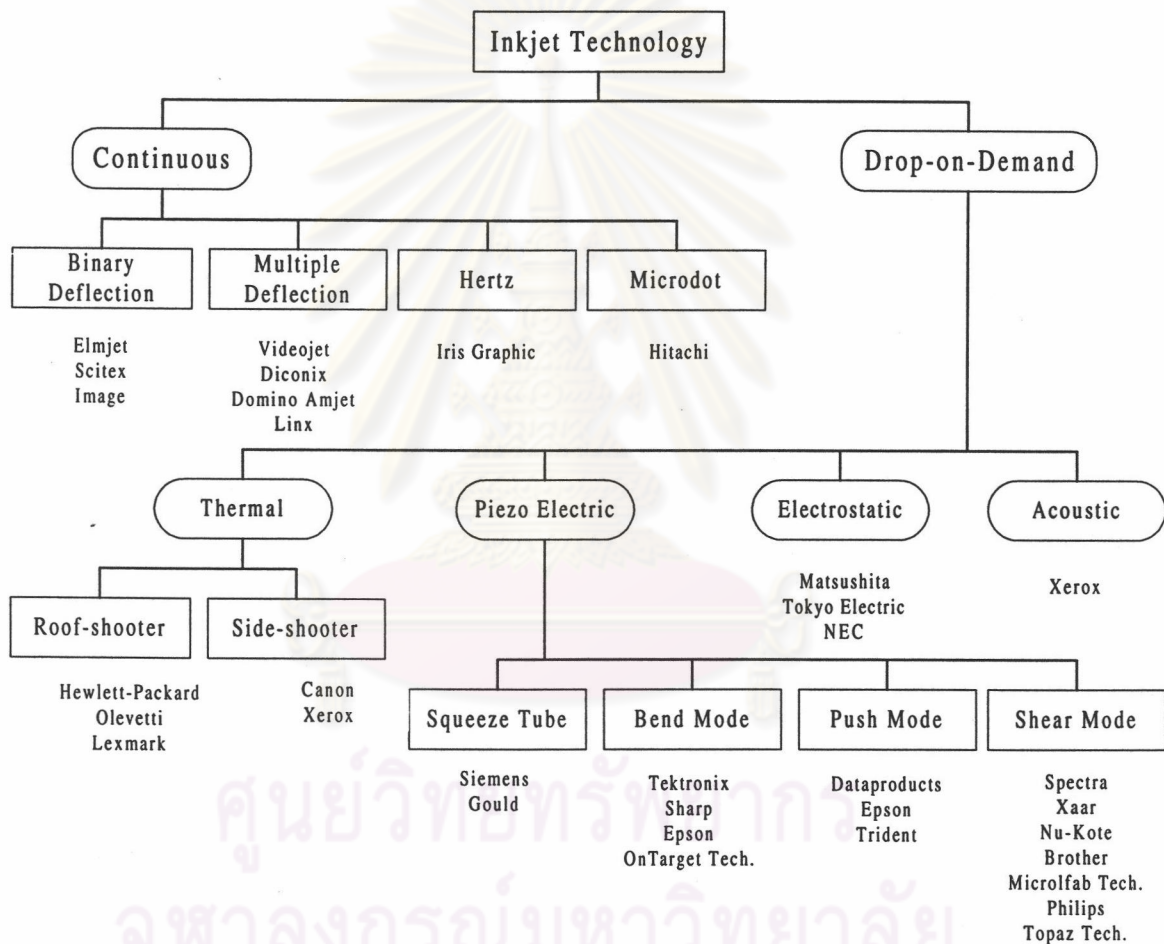


Figure 2-1 Inkjet technology map<sup>3</sup>

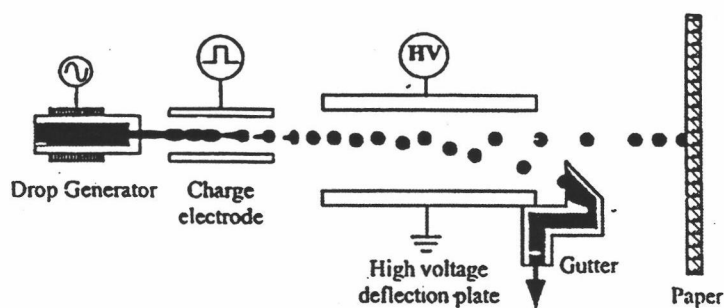


Figure 2-2 Binary deflection continuous inkjet system<sup>3</sup>

Another form of continuous inkjet printing is known as Hertz technology, which is shown in Figure 2-3. This printing form is characterised by the use of extremely small nozzles and hence very small drops. Each spot on the paper is produced from a group of these small drops, and by varying the number of such small drops a grey level is made possible. Rather higher print quality can be achieved compared with other inkjet systems but there are difficulties with such small nozzles and droplets.

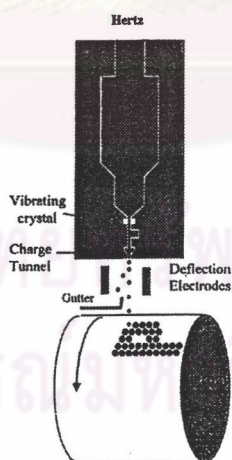


Figure 2-3 Hertz technology inkjet system<sup>6</sup>

### 2.1.1.2 Drop-on-demand or impulse inkjet printer

The majority of activity in inkjet printing today is in the drop-on-demand (DOD) methods. The technology can be categorized into four major methods: thermal, piezoelectric, electrostatic and acoustic inkjet. Both the electrostatic and acoustic inkjet are still in the development stage. Most of the DOD printers on the market today are using either thermal and piezoelectric principle.

In the piezoelectric inkjet, the ink droplets are ejected from the print head nozzles when the driving pulse, which is generated by a piezoceramic deformation, is applied. At rest, the force of hydrostatic pressure causes the ink to form a concave meniscus. One end of the ink chamber may be in the form of a diaphragm, the other end open as an orifice. An electrical driving pulse acts on the chamber, causes the volume of ink to decrease. The ink droplet is then directly emitted from the nozzle onto a print substrate so that the deflection part of ink droplets is not required to form an image. The driving technology can be classified into four main types: squeeze, bend, push, and shear mode as shown in Figure 2-4.

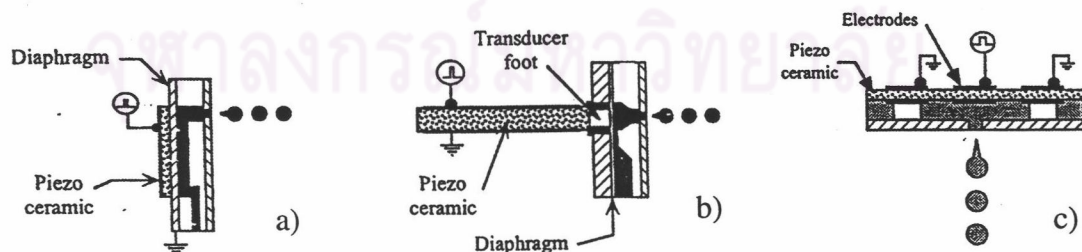
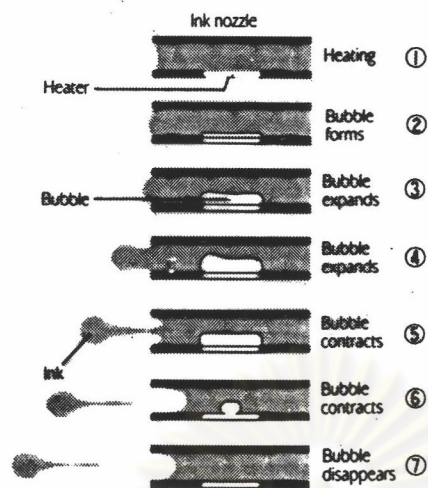


Figure 2-4 Piezoelectric inkjet design: a) bend mode, b) push mode, c) shear mode<sup>3</sup>





**Figure 2-5** Thermal inkjet process<sup>5</sup>

The variation on drop-on-demand printers is a thermal inkjet printer. Figure 2-5 shows the schematic diagram of a working principle of a thermal inkjet printer. A piezo-electric crystal is replaced by a heating element in each nozzle. When the heating element reaches approximately 300 °C, a gaseous bubble is formed due to the ink vaporization. The volume of ink in the ink chamber is decreased. A small volume of ink is ejected from the nozzle and projected toward the print substrate. A disadvantage of this method is that the dye in the ink would precipitate and build up at the internal surface of the print element. This phenomenon is called “Kogation”, the build up of decomposed ink on the resistors.

### 2.1.2 Physical properties of inkjet ink<sup>3-5</sup>

The physical properties of inkjet ink have to meet the requirement of a printing process. They do not only dictate the quality of the printed image, they also determine the drop ejection characteristic and the reliability of the printing system.

#### 2.1.2.1 Viscosity

The inkjet ink viscosity is an important property for jetting the ink from the print nozzle. It is used as a starting point for formulating an inkjet formula. The high viscosity ink cannot flow steadily through the narrow ink supplied tube or the sponge cartridge. These also cause the non-uniformity of ink droplets in case of a continuous inkjet printing. The viscosity range of inkjet ink is around 2 to 8 cP depending on the process.

#### 2.1.2.2 Surface tension

Surface tension is one of the important factors for the uniform droplet formation in continuous inkjet printers. In case of DOD printers, this property affects the regulate control of the concave meniscus to hold ink in the system. If the water-based inkjet ink has a lower surface tension, it is easy to be foamed. These air bubbles cause a non-smooth flow in an ink supplied tube. Surface tension also influences the dot spreading on the surface of the printed substrate. The range of surface tension is around 22-45 mN/m.

### 2.1.2.3 Conductivity

The conductivity of inkjet ink is higher than 1000  $\mu\text{S}/\text{cm}$  at 25 °C. In the case of a continuous inkjet printer, the ink droplet must be able to accept an applied voltage. The charged and uncharged droplets fly to the different trajectory when they pass through the high voltage field. Because of the charge repelling, the charged droplet is deflected into the gutter. For the uncharged droplet, it passes directly to the printed surface to form an image. However, in some printing processes, the destination of the charge/uncharged droplets is alternated.

### 2.1.2.4 pH

The pH of inkjet ink has an influence on many factors of the ink such as hue, pigment dispersion and dye solubility. The lower pH of the anionic pigmented ink causes the pigment coagulation in a storage container or clogging in the print nozzle. The orifice of some inkjet systems may be corroded if the pH of the ink is highly acidic.

### 2.1.2.5 Particle size

The particle size of any materials in the ink has to be smaller than 1 micrometer. The large particle size in the ink leads to the jet instability, misdirection or clogging the nozzle. These problems are usually found in the pigmented ink.

### 2.1.3 Inkjet ink composition<sup>3-5</sup>

Inkjet ink mainly consists of a colorant in a liquid medium. Besides these essential ingredients, some binder resins and additives are added for meeting the special required property of inkjet ink.

**Table 2-1** Water-based inkjet ink composition<sup>3</sup>

Component	Function	Concentration (%)
Deionized water	Aqueous carrier medium	60 - 90
Water soluble solvent	Humectant, viscosity control	5 - 30
Colorants	Provides color	1 - 10
Surfactant	Wetting, penetrating	0.1 – 10
Biocide	Prevents biological growth	0.05 – 10
Buffer	Controls the pH of ink	0.1 – 0.5
Other additives	Chelating agent, defoamer, solubilizer etc.	> 1

#### 2.1.3.1 Liquid medium

The role of liquid medium is to transfer ink from the printer to the surface of a printed substrate. The majority of inkjet inks, which are widely used in home and small office inkjet printers, are water-based ink. However, they are not only comprised of water but some humectants are also added to formulate the inks. Some typical humectants are glycol, glycerol, and glycol ether. The purposes of adding some humectants are to control the evaporation of the ink in the print head, adjust the drying speed and act as a dye solubilizer or a pigment dispersant. If the ink contains a



higher amount of low volatility humectant, it will slow down the drying process. If the quantity of humectant is decreased, the orifice nozzle may be clogged.

### 2.1.3.2 Colorants

Two types of colorant, dyes and pigments, are used in inkjet formulation. Dyes are generally used in small office-home office (SOHO) inkjet printers or an indoor application, but pigments are preferred to use for outdoor application and wide format inkjet printers.

A pigmented inkjet ink generally shows high weatherability such as light fastness and water fastness. The disadvantages of using a pigmented ink are low transparency and small color gamut. The pigment also must be homogeneously dispersed in the medium in order to maintain the particle size of the pigmented inkjet ink in the range of 0.1-1.0 micrometer. The other problem of pigmented inkjet ink is low storage stability. Pigment is sometime coagulated and precipitated when the ink is kept for a long time.

Dye molecules used in inkjet ink are normally soluble in water. Therefore, the water fastness of most dye-based inkjet inks is poor. The ink is also reactive to humidity, oxidative molecule like singlet oxygen, ozone and  $\text{NO}_x$ . Moreover, the light fading is a serious problem for the dye-based inkjet inks thus they are not suitable for outdoor application. However, dye-based inkjet inks dominate the pigmented inkjet inks in some ways. The dye-based inkjet inks are brighter and more transparent than pigmented inkjet inks. They produce a wide range of color and bigger color gamut volume. They are more cost effective than pigments because of their

greater coloring power. The selection of dye molecules is also plenty because more than 5000 dyes are commercially available; while the pigment choice is limited since less than 400 commercially pigments are available.<sup>7</sup> On the other hand, dyes are easier to handle. Storage stability of dye-based inkjet inks is long with less coagulation and precipitation.

#### 2.1.3.3 Binder resin

Inkjet inks normally contain a small amount of binder (0-10 % depending on the type of resin and print application) because of the viscosity limitation. When the level of resin in the ink is raised up, the viscosity is increased. This may cause the jet instability and clogged nozzle. In some application like metal and film printing, a binder is added into the ink for meeting some requirements such as increasing adhesion, gloss, abrasive and water-resistant. The types of resin used in the inkjet inks are, for example, cellulose derivative, gelatin, poly(vinyl alcohol) and acrylic resin.

#### 2.1.3.4 Additives

Defoamer, dispersant, surfactant, light and heat stabilizers, plasticizer are added into an inkjet ink to adjust the properties to meet the requirement.

#### 2.1.4 Inkjet recording media<sup>3,8</sup>

Inkjet ink usually contains a high amount of water or organic solvents. So the high absorbency of recording media is required. The conventional recording media are the ink-receiving layer formed by a swelling polymer. These media have some disadvantages like insufficiently transparent and low absorption property. To improve the recording media, alumina hydrate in a boehmite structure is used as an ink absorbent in a coating layer. A boehmite structure is obtained by the hydrothermal treatment of an aqueous slurry of a boehmite-forming compound such as gibbsite. The advantages of using alumina hydrate in the boehmite structure are high dye absorption, high ink absorbency and high transparency. The ratio of the boehmite to binder resin is in the range from 5:1 to 20:1 by weight.<sup>9</sup> A water soluble polymer such as poly(vinyl alcohol) is preferred to use as a binder resin.

The other pigment widely used in an ink receptive layer is silica.<sup>10</sup> Some advantages of using silica are low price, wide variety, high ink absorptivity and good coloration by dyestuff. However, the fixing ability of dye in a silica layer is not high. Some mordant polymers and/or metal compounds are required to improve the fixing property. The mordant polymer is composed of cationic substituents, typically quaternary amines. The quaternary amines fix the aqueous dyestuffs having an anionic nature by cation-anion aggregation. Although the mordants can fix colorants, they show worse effect on the light fastness of the dyestuffs.



## 2.1.5 Photodegradation process<sup>11</sup>

### 2.1.5.1 Photophysical process<sup>12</sup>

When a photon is absorbed by a molecule at the singlet ground state ( $S_0$ ), the molecule is transformed into an excited state ( $S_1, S_2, S_3\dots$ ). This energy-rich molecule is not stable, therefore it returns to the more stable state by energy transition. This process can be explained by the Jablonski diagram (as shown in Figure 2-6). The singlet excited state molecule can directly return to the ground state by converting the excess energy into radiation, which is so-called fluorescence. Sometimes a molecule in the higher excited state can reduce energy and go to the lower excited state (e.g. from  $S_3, S_2$  to  $S_1$  or  $T_3, T_2$  to  $T_1$ ) without emitting any radiation. This is called internal conversion (IC). Moreover, Intersystem crossing (ISC) from the lowest singlet excited state to the triplet state can occur. A molecule in this triplet state can be excited to the higher triplet state by absorbing a photon. Beside that, it can return to the ground state by releasing the energy in the form of radiation, which is called phosphorescence.

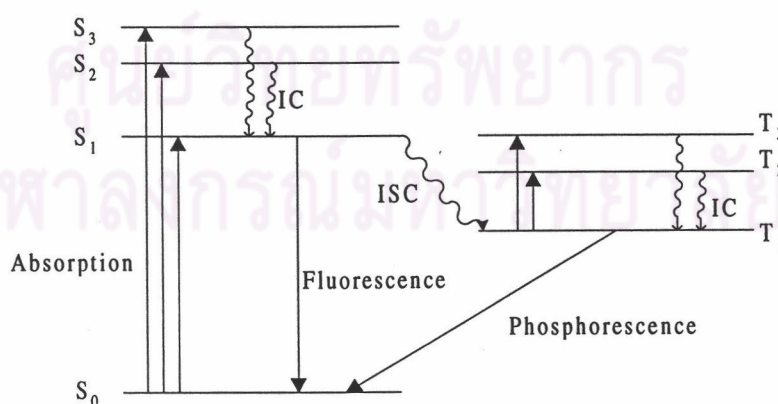
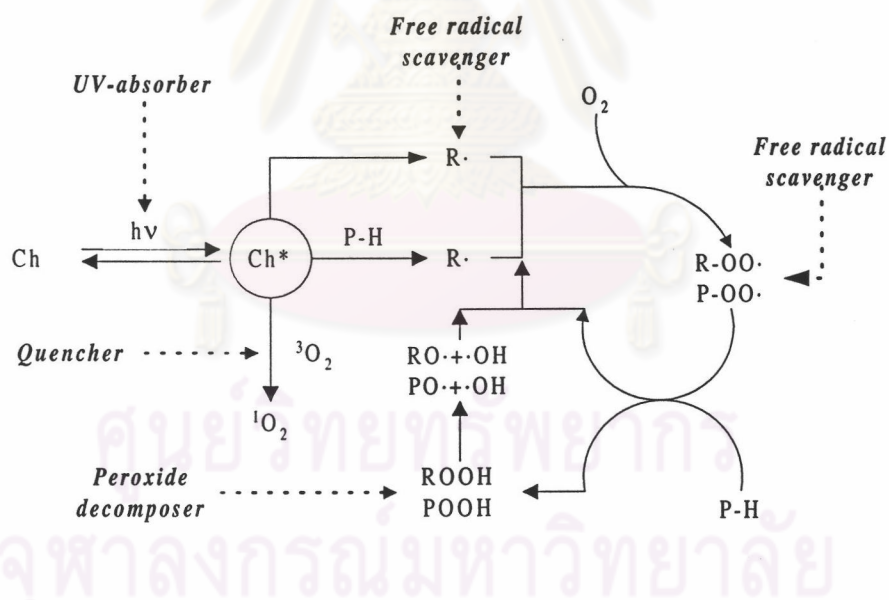


Figure 2-6 Jablonski diagram<sup>11</sup>



### 2.1.5.2 Light stabilization<sup>11</sup>

The photo-oxidation is occurred when a molecule absorbs light. The molecule must contain groups capable of absorbing electromagnetic radiation which then causes electron transfer in the molecule. These groups are called chromophores. Figure 2-7 shows the schematic diagram of photo-oxidative degradation of a chromophore and protection ways. The absorption of light by a chromophore convert this into an excited state ( $\text{Ch}^*$ ). Essentially,  $\text{Ch}^*$  has four possibilities of further reactions:



**Figure 2-7** Schematic diagram of photo-oxidative degradation and protection ways<sup>11</sup>

a) return to the ground state via fluorescence or emitting radiation with less energy or less deactivation in a form of heat,

b) decomposition into radicals, followed by a continued reaction with the substrate (polymer.) and/or oxygen,

c) formation of radicals through removal of hydrogen from the substrate,

d) energy transfer (e.g. to oxygen, which leads to the formation of singlet oxygen  $^1O_2$ ).

The continued reaction according to option a) does not endanger the polymer. Continued reactions according to options b) to d) will in any case damage the polymer or at least decisively alter its properties.

At the same time however, options a) to d) show us the way to protect the polymer against the harmful effects of UV light as follows:

A) Filtering out the harmful UV light before  $Ch^*$  start to form  $Ch^*$  (UV absorber),

B) Eliminating the excited state after a formation of  $Ch^*$  by a suitable acceptor (Quencher),

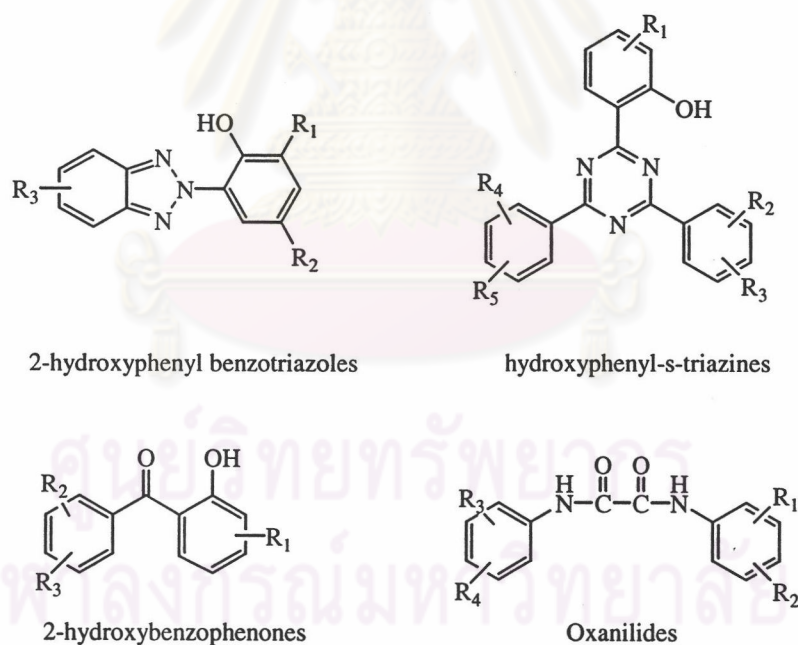
C) If radicals have already formed, intercepting these radicals before the reaction has a chance to continue. (Free radical scavenger),

D) After a formation of peroxides, decomposing them by a means of suitable peroxide decomposer.

### 2.1.5.3 Light stabilizer<sup>11</sup>

#### a. UV absorber

The main function of a UV absorber is to absorb UV radiation in the region between 290-350 nm (UVA spectrum) and convert it into harmless heat. Absorbed energy is converted into vibrational and rotational energy of molecule constituents. This process must take place more rapidly than the corresponding reaction within the other molecule. The UV absorbers (as shown in Figure 2-8) are, for example: 2-hydroxyphenyl benzotriazoles, 2-hydroxybenzophenones, hydroxyphenyl-s-triazines, and oxalanilides



**Figure 2-8** The chemical structure of most important UV absorber groups<sup>11</sup>

Each of UV absorber groups can be characterized by a typical absorption spectrum (Figure 2-11) and transmission spectrum.

The effectiveness of UV absorbers can be determined by the Beer-Lambert Law as in Equation. 2.1:

$$E = A = \log \frac{I_0}{I} = \epsilon \times c \times d \quad (2-1)$$

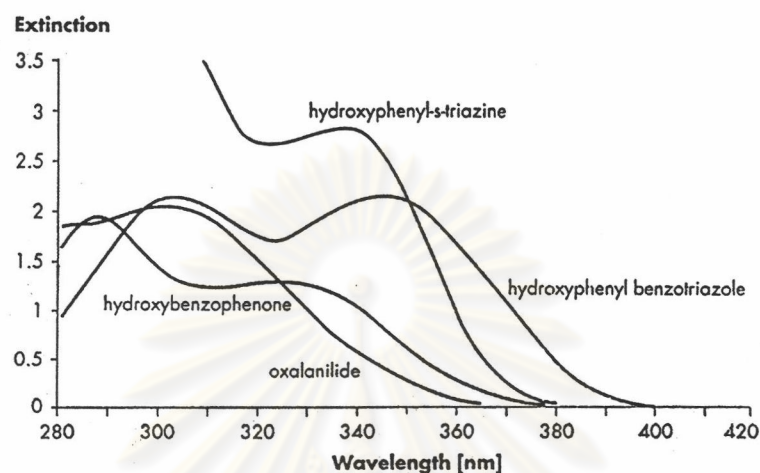
where

- $E$  = extinction
- $A$  = absorbance
- $I_0$  = intensity of incident light
- $I$  = intensity of emergent light
- $\epsilon$  = extinction coefficient [l/mol cm]
- $c$  = concentration [mol/l]
- $d$  = thickness (film, substrate, cell) [cm]

The extinction depends on the wavelength, the extinction coefficient ( $\epsilon$ ), the concentration ( $c$ ) of the UV absorber and the film thickness ( $d$ ). The higher the extinction, the more UV light will be screened and the greater will be the stabilization effect. The extinction coefficient  $\epsilon$  is specific for each molecule and dependent on wavelength, i.e. it is a constant for a given UV absorber. This means

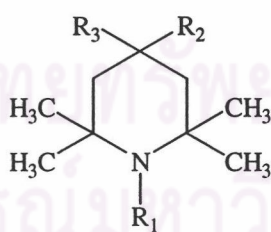


that the stabilizing effect of a given UV absorber can be altered by varying the concentration and/or the film thickness.



**Figure 2-9** Absorption spectra of different UV absorber groups,  $c = 1.4 \cdot 10^{-4}$  mol/l in chloroform (a 1-cm cell)<sup>11</sup>

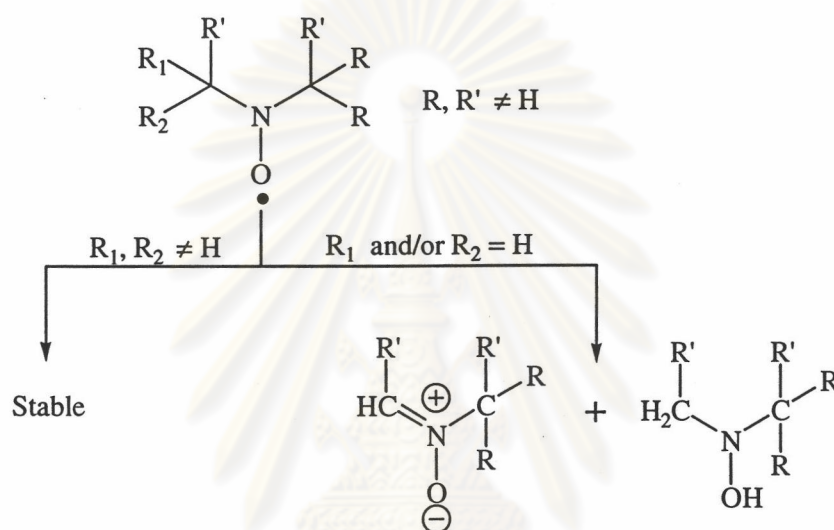
#### b. Hindered Amine Light Stabilizer (HALS)



**Figure 2-10** General structure of sterically hindered amine based on 2,2,6,6-tetramethylpiperidine<sup>11</sup>

For hindered amine light stabilizers, amines are the derivatives of 2,2,6,6-tetramethylpiperidine (as shown in Figure 2-12) and are generally referred

to as HALS. Under photo-oxidative conditions, HALS are transformed into the corresponding stable nitroxyl radical. Nitroxyl radicals are stable only if they do not contain active substituents, such as hydrogen atoms, in the alpha position. Hydrogen atoms in the alpha position lead to disproportionation of the molecule into nitrons and hydroxylamine, as shown diagrammatically in Figure 2-11.



**Figure 2-11** Effect of substitution in the alpha position to the nitroxyl group on the stability of nitroxyl radicals.<sup>11</sup>

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## 2.2 Literature Reviews

A critical problem in inkjet printing is the image permanence especially the low light fastness property. Therefore, the light induced fading is the main focal aspect in recent year researches. There are many topics focusing on factors affecting the light fastness of inkjet prints. These factors can be divided into three composite factors, ink, media, and service environment.

The inkjet ink composition imposes the important role in light fastness property of inkjet ink. Colorant, the most important ingredient exhibits the most impact on the light fastness of the ink. Dye structure governing the dye aggregation gives the higher light fastness.<sup>13</sup> As an example, the symmetrical structure of dye molecules always shows the good light fastness.

The variation of the ink formulation can either increase or decrease its light fastness property. For example, an addition of some types of resins/binders accelerates the photodegradation of dye.<sup>14</sup> In case of pigment, the polymer containing alkyl groups, such as, ethylcellulose shows increasing photostability on the yellow pigment. Apart from the binder, **Lee et al.**<sup>1</sup>, in 1997 studied the improvement on light fastness of inkjet ink using the additive system from Kimberly-Clark. This additive is named  $\beta$ -Cyclodextrin–transorber colorant. Adding this additive in an ink formula and a coated paper formula show a significant decrease in light-induced fading.

It is well known that the light fastness of pigment is always better than dye, but the color gamut of pigmented inkjet ink is usually smaller than that of dye-based ink. Therefore, a method to improve both properties is to combine pigment colorants

into the dye-based ink. **Ortalano**<sup>15</sup> explained the hybrid system of inkjet colorants by dispersing aqueous pigments with common inkjet dye colorants. The inkjet ink formulated with this hybrid dispersion exhibited both dye and pigment properties, such as a wide color gamut, high optical density, high surface tension, high water and light fastness.

As mentioned above, the second main factor, which influences the light fastness of the ink is the media. Media properties such as pH, the chemical composition of the media surface, the location of colorant within the media, the formulation additives and the physical form of the colorant affect the light fastness of inkjet prints.<sup>16</sup> For example, **Wang et al.**<sup>17</sup> experimented the light fastness of large format inkjet media. The results show that light fastness of the prints was dependent on the testing environment. The fading rate in a real environment is different from that in the accelerated fading test of a fade-o-meter. Some nitrogen-containing polymeric resins such as PVP and PEOX used as the coating media have poor light fastness. Adding inorganic salts in the media coating can improve the light fastness of the inkjet prints.

For the third main factor of service environment, the influence of light source irradiation, light intensity, level of humidity, and the oxidative gas affect the image permanence. That is the intensity of light affects the light induced fading of inkjet ink. **Bugner and Suminski**<sup>18</sup> described the filtration and reciprocity effects on the fading rate of inkjet photographic prints. Use of unfiltered or glass-filtered, high intensity fluorescent lights to accelerate the light fading of inkjet photographic prints was not a valid predictor of light fading under the ambient conditions. Because the presence of



strong UV-emission fluorescent light caused inkjet dye fading at different rates and possibly by different mechanisms. The correlation with Plexiglas-filtered fluorescent light, which removes most of the UV radiation, is quite poor. The fading rate of filtered high intensity exposure condition was 2 to 3-times faster than that filtered at low intensity exposure conditions. The inkjet inks on the porous receivers were more sensitive to reciprocity effects than those on the non-porous receivers. In addition to the light intensity, the type of light exposure is directly related to the light fastness of the inkjet prints. For example, the photo induced fading by solar light is higher than that by fluorescent light, although the solar light intensity equals fluorescent light intensity.<sup>19</sup>

The level of humidity is also an indicating factor the image permanence of the inkjet ink. At a high humidity condition, inkjet ink composed of a water soluble dye can diffuse and migrate to the medium surfaces. These effects cause a loose aggregation of dye molecules. The loose dye aggregation increases the direct attack of each dye molecule by photon. Therefore, photooxidation of dye molecules at the high humidity condition is greater than that at low humidity condition. In 2000, **Goodhart and Wilhem**<sup>20</sup> studied the humidity-induced color change and ink migration effect in inkjet photographic quality in a real world environmental condition. Three systems of ink-media for photographic inkjet printing were examined for the humidity fastness at the high humidity levels. The system A, four-manufacturer standard dye-based inks (CMY) and premium photo papers, show a significant dye migration and image bleeding in a short time at humidity above 50 %RH. Especially in the magenta dye, it causes the large color change to the lower density magenta and red patches. The system B was the manufacturer recommended six-ink formulations (including light

cyan and light magenta) and a coated matte-finish photo paper, which is marketed as photo printer. This system was reasonably stable at 70% RH, but high mobility of the yellow dye occurs within the 70-80% RH range. The system C, six-pigmented ink formulation and semi-glossy photo paper, shows excellent humidity fastness. The maximum  $\Delta E$  was predicted and found to remain less than 5 over one hundred years at 80% RH.

Apart from the light fastness, there are other important issues in inkjet printing.<sup>21</sup> Water fastness of inkjet image is a major issue for water-based inkjet inks. The ink chemists have to design the systems that have good operate ability and solubility/dispersability in the ink, but once on the paper, they do not re-dissolve or disperse in contact with water. Two successful methods from Avecia are the pH dye switching dye mechanism, and zwitterionic type mechanism. There is an observation in inkjet prints, which is called catalytic fading. Magenta dyes especially H-acid dye and gamma acid dye are quickly faded when printed a blue shade with phthalocyanine cyan dyes. The present method to solve this problem is to make high resistant gamma acid dyes or make phthalocyanine dye that is not sensitized by oxygen. The inkjet prints can be faded by the increased level of ozone or a long exposure time to ambient level of ozone, but the other factors like humidity, temperature and media type also affect the ozone fading.