พอลิเมทิลเมทาคริเลตโคเมทาคริลิกแอซิดสำหรับแม่พิมพ์ลิโทกราฟีไวแสงยูวีที่สามารถสร้างภาพในสารละลายเบส

นางสาวสุธีรา เทสสิริ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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POLY(METHYL METHACRYLATE-*CO*-METHACRYLIC ACID) FOR UV-SENSITIVE AQUEOUS-BASE DEVELOPABLE LITHOGRAPHIC PLATE

Miss Suteera Tessiri

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Program of Petrochemistry and Polymer Science
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By	Miss Suteera Tessiri
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Thesis Advisor	Professor Suda Kiatkamjornwong, Ph.D.

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สุธีรา เทสสิริ : พอลิเมทิลเมทาคริเลตโคเมทาคริลิกแอซิดสำหรับแม่พิมพ์ลิโทกราฟีไวรังสียูวีที่สามารถสร้างภาพได้ในสารละลายเบส (POLY(METHYL METHACRYLATE-*CO*-METHACRYLIC ACID) FOR UV-SENSITIVE AQUEOUS-BASE DEVELOPABLE LITHOGRAPHIC PLATE) อ.ที่ปรึกษา : ศ.ดร. สุดา เกียรติกำจรวงศ์; 174 หน้า. ISBN 974-13-1144-3.

งานวิจัยนี้ได้สังเคราะห์โคพอลิเมอร์ของเมทิลเมทาคริเลตและเมทาคริลิกแอซิด โดยวิธีฟรีแรดิคัลพอลิเมอไรเซชัน โดยมีเบนโซอิลเพอร์ออกไซด์ทำหน้าที่เป็นตัวริเริ่มปฏิกิริยา ได้ศึกษาอัตราส่วนระหว่างมอนอเมอร์ทั้งสองและเวลาในการทำปฏิกิริยาต่อผลการเกิดปฏิกิริยา ตรวจสอบสมบัติของพอลิเมอร์โดยสมบัติทางความร้อนตรวจสอบด้วย DSC, น้ำหนักโมเลกุลเฉลี่ยและค่าการกระจายตัวของน้ำหนักโมเลกุลด้วย GPC, อัตราส่วนของ CHO ด้วย EA และหมู่ฟังก์ชันด้วย FT-IR และ NMR จากนั้นนำโคพอลิเมอร์นี้มาใช้เป็นสารยึดในสูตรการเคลือบผิวไวแสงยูวี โดยนำโคพอลิเมอร์ที่มีอัตราส่วนระหว่างมอนอเมอร์ทั้งสองชนิดแตกต่างกันมาผสมกับ TPGDA และ TMPEOTA, Darocur 1173 และ Darocur BP และสารสี จากนั้นนำมาเคลือบบนแผ่นอะโนไดซ์อะลูมิเนียมด้วยวิธีการเคลือบแบบเหวี่ยงให้ผิวหน้าเรียบ เคลือบทับด้วยสารละลาย PVA แล้วนำไปฉายรังสียูวีผ่านฟิล์มต้นฉบับซึ่งเป็นแถบควบคุมมาตรฐาน ที่เวลาฉายแสงต่าง ๆ กันเพื่อหาเวลาฉายแสงที่เหมาะสม ล้างแม่พิมพ์ด้วยน้ำยาสร้างภาพต่าง ๆ เพื่อหาน้ำยาสร้างภาพที่เหมาะสม แม่พิมพ์ที่ได้นำมาประเมินคุณภาพแม่พิมพ์โดยเปรียบเทียบกับแถบควบคุมมาตรฐาน คือ หาเวลาฉายแสงที่เหมาะสมและเปอร์เซ็นต์โคพอลิเมอร์ที่เหมาะสมในการใช้เป็นสารยึดโดยดูจากเปอร์เซ็นต์พื้นที่เม็ดสกรีนร้อยละ 40, 50 และ 60, หาความละเอียดที่เหมาะสมจากไมโครไลน์, หามุมสัมผัสระหว่างน้ำกับน้ำมันบนผิวหน้าแม่พิมพ์ และทดสอบแรงยึดของผิวหน้าด้วยเทปมาตรฐาน.

ภาวะที่เหมาะสมสำหรับการเตรียมสารยึด คือไอโซโพรพิลแอลกอฮอล์ร้อยละ 75 โดยน้ำหนัก มอนอเมอร์ร้อยละ 25 อัตราส่วนระหว่าง MMA:MAA 80:20 เบนโซอิลเพอร์ออกไซด์ร้อยละ 1 โดยน้ำหนัก อัตราการกวน 295 รอบ/นาที อุณหภูมิและเวลาในการทำปฏิกิริยาคือ 70°ซ. และ 16 ชม. ตามลำดับ โคพอลิเมอร์มีลักษณะใสและแข็งคล้ายแก้วและมีสมบัติดังต่อไปนี้ อุณหภูมิสภาพแก้ว 163.4°ซ. น้ำหนักโมเลกุลเฉลี่ย 1×10^{6} แม่พิมพ์ที่ได้จากสารยึดโคพอลิเมอร์ที่เหมาะสมนี้นำมาประเมินคุณภาพเพื่อหาค่าการฉายแสงที่เหมาะสม สมบัติของผิวและทดสอบแรงยึดด้วยเทป ผลปรากฏว่าสูตรสารเคลือบนี้สามารถนำมาใช้เป็นสารเคลือบแม่พิมพ์ออฟเซตเนกาทีฟซึ่งสามาถสร้างภาพได้ในสารละลายเบสชนิดน้ำ งานวิจัยได้อภิปรายผลของตัวแปรต่อคุณภาพของผลิตภัณฑ์ที่ได้

หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา ....
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4172502823 : MAJOR POLYMER SCIENCE

KEYWORD: POLY(METHYL METHACRYLATE-*CO*-METHACRYLIC ACID) / FREE RADICAL POLYMERIZATION / MMA / MAA / IPA:MEK / LITHOGRAPHIC PLATE / DEVELOP / AQUEOUS-BASE DEVELOPER / TPGDA / TMPEOTA / DAROCUR 1173 / DAROCUR BP / EXPOSURE / NEGATIVE WORKING PLATE

SUTEERA TESSIRI : POLY(METHYL METHACRYLATE-*CO*-METHACRYLIC ACID) FOR UV-SENSITIVE AQUEOUS-BASE DEVELOPABLE LITHOGRAPHIC PLATE. THESIS ADVISOR : PROF. SUDA KIATKAMJORNWONG, Ph.D., 174 pp. ISBN 974-13-1144-3.

Syntheses of the copolymer of methyl methacrylate and methacrylic acid were carried out by free-radical polymerization, in the presence of benzoyl peroxide (BPO) as an initiator. The effects of the monomer ratio and reaction time on polymerization were investigated. Thermal properties were investigated by DSC, the Mw, Mn and polydispersity by GPC, the CHO composition by EA, and the characteristic functional groups by FT-IR and NMR. These copolymers were used as the binder of UV coating formulation. Different ratios of the copolymer were mixed with TPGDA and TMPEOTA, Darocur 1173 and Darocur BP, and anthraquinone. The photosensitive coating was coated onto the anodized aluminium substrate by spin coating, which formed a smooth film and was then overcoated by PVA solution. Plate control wedge was assembled on the plate, and exposed to UV radiation at different exposure time. The exposed plate was developed in an alkaline developer. The resulting plate was evaluated for reproduction properties at 40, 50 and 60% dot areas, resolution at microline, and wettability by contact angle between image/non-image areas, and adhesion test by a standard tape.

The optimum condition for the binder preparation was 75% w/w isopropyl alcohol, 25% w/w monomer with a ratio of MMA:MAA at 80:20, 1% w/w BPO, the agitation rate was 295 rpm for the reaction temperature and time of 70°C and 16 hours, respectively. The copolymers were transparent and rigid like a glass and had the following properties: the glass transition temperature (Tg) 163.4°C; average molecular weight of 1×10^6. The plates were evaluated in terms of appropriate exposure, surface properties and adhesion tape test. The result indicates that the formulation chemistry can be used for coating of a negative working offset plate that is developable in aqueous alkaline developer. This research elucidates the effects of parameters on the product qualities.

Department	-	Student's signature…………………………………
Field of study	Petrochemistry and Polymer Science	Advisor's signature…………………………………
Academic year	2001	

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ABBREVIATIONS

MMA : methyl methacrylate
MAA : methacrylic acid
PVA : poly(vinyl alcohol)
TPGDA : tripropylene glycol diacrylate
TMPEOTA : trimethylol propane ethoxylate triacrylate
P(MMA) : poly(methyl methacrylate)
P(MAA) : poly(methacrylic acid)
BP : benzophenone
BPO : benzoyl peroxide
HIPK : 2-hydroxy-2-methylpropiophenone
KBR : potassium bromide
IPA : isopropyl alcohol
THF : tetrahyldrofuran
d_6-DMSO : d_6-dimethylsuphoxide
UV : Ultra Violet
EB : electron beam
PCW : plate control wedge
M_w : the weight average molecular weight
M_n : the number average molecular weight
MWD : the molecular weight distribution
PDI : the polydispersity index

ABBREVIATIONS (continued)

M_i : molecular weight of polymer in fraction i

W_i : weight of the polymer in fraction i

i : fraction number

N_i : the number of molecules in fraction i

d : polydispersity index

Tg : glass transition temperature

k_p : rate constant of propagation reaction

k_t : rate constant of termination reaction

r_1 : the reactivity ratios for monomer MMA

r_2 : the reactivity ratios for monomer MAA

D_r : %dot area of the reproduction

D_o : %dot area of the original film (UGRA-like plate control wedge)

τ : shear stress

F : force

A : unit area

η : viscosity

D : shear rate

γ : surface tension

γ_s : the surface tension of solid

γ_l : the surface tension of fluids

γ_c : the critical wetting tension of the solid surface

ABBREVIATIONS (continued)

γ_{sv} : the solid-vapour interfacial tension

γ_{sl} : the interfacial tension between phases solid and liquid

γ_{lv} : the interfacial tension between phases liquid and vapour

γ_{ij} : the interfacial tension between phases *i* and *j*

γ^{p} : the polar contribution to the surface energy

γi : the dipole induced dipole contribution to the surface energy

γ^{d} : the dispersion force contribution to the surface energy

γ_1^{d} : the dispersion force components of the surface energy of material 1

γ_2^{d} : the dispersion force components of the surface energy of material 2

π_e : the spreading pressure

r : roughness factor

θ : the equilibrium contact angle

θ_a : advancing contact angle

θ_r : receding contact angle

θ_{ac} : the actual contact angle

θ_{ap} : the apparent contact angle

θ_w : the Wenzel angle

θ_y : the Young angle

ABBREVIATIONS (continued)

H : contact angle hysteresis

W_a : adhesion work

W_c : cohesion work

α : alpha

β : beta

μm : micron

b.p. : boiling point

f.p. : freezing point

m.p. : melting point

rpm : revolution per minute

DSC : Differential Scanning Calorimeter

FT-IR : Fourier Transform Infrared Spectrometer

NMR : Nuclear Magnetic Resonance

GPC : Gel Permeation Chromatography

EA : Elemental Analysis

CHAPTER I

INTRODUCTION

1.1 Scientific Background and Rationale

Throughout the 1970's there was a growing awareness that Ultra Violet(UV) and Electron Beam(EB) curing represented a commercially viable and efficient method of curing inks and coatings for wood, paper and board, metal, plastics and other substrates.

The oil crisis of the mid-seventies was followed by ever escalating costs of conventional energy sources and petrochemical derived solvents. This led to renewed activity in radiation curing as a clean, efficient and cost effective alternative to the energy intensive air drying of conventional solvent based cloatings.

Some of the major benefits to be gained from UV curing are listed below:

- Lower energy consumption than thermal curing;
- Smaller space requirements, resulting in a more efficient compact operating environment;
- Faster cure speeds than thermally cured systems;
- Instant start and shut down;
- Lower overall costs;
- 100% solid coatings;
- Reduced fire risks (freedom from volatile solvents). Heat sensitive substrates can be printed or coated without degradation.

Early UV ink and lacquer formulations tended to suffer from the disadvantage of possessing a relatively high order of skin irritancy which led to operator resistance to the new products in some areas of the coating industry.

However, the development of second generation products, which possess a lower order of skin irritancy, has enabled current formulations to become widely accepted on a commercial scale and radiation curing is now a firmly established and rapidly growing sector of the coatings industry.

UV general coating formula comprises of the following materials:

- Prepolymer or binder
- Reactive diluent
- Photoinitiator system
- Pigment
- Additives

UV cured coatings require photoinitiators to initiate a free radical mechanism. These are not necessary for EB coatings. Since the photoinitiators are in general quite costly, it is usual for EB coatings to be lower in price than comparable UV coatings. Thick pigmented coatings are more easily cured using EB than UV curing since the pigments often absorb some of the UV light necessary for activating the photoinitiators.

The capital cost for EB equipment is considerably higher than that for UV equipment and as a consequence EB coatings tend to be used in specific application areas, such as film/film laminating and inks for food packages, where UV curing would not be practicable [1]. So in this research we choose the UV chemistry to be the source for making the lithographic plate.

Lithography is the process of printing from especially prepared surfaces, some areas of which are capable of accepting lithographic ink, whereas other areas, when moistened with water, will not accept the ink. The areas which accept ink form the printing image areas and the ink-rejecting areas form the background areas [2].

Polymers and plastics form an extremely important class of materials which enjoy common application in everyday life as well as in printing materials. They find widespread and increasing usage as substrates for printing and in flexible packaging industry[3].

Photopolymer plates in general rely on the chemical polymerization of monomers or the cross-linking of unsaturated long-chain polymers or prepolymers under the influence of ultraviolet light. The desired result is a solubility differential between the exposed and unexposed parts of the system, which can then be developed by washing out the non-image areas of the printing plate [4].

The requirements for photosensitive systems for printing plates are that they should respond to a reasonable exposure dose within a suitable exposing time based on the reciprocity law, that the exposure should induce some useful change such as one of solubility and that, for lithographic plates, the image areas must be oleophilic or easily made so [4].

Methyl methacrylate (MMA) and methacrylic acid (MAA) copolymers are widely used as filmforming materials, bindings in the production of paints and varnishes. Then we used these synthetic copolymers to be the prepolymer or binder of the formulation for UV coating on the aluminium substrate.

1.2 Objectives of the Research Work.

1. To find appropriate conditions to synthesize the copolymer of methyl methacrylate and methacrylic acid forming the binder for a lithographic plate.

2. To study the effect of molecular weight and polydispersity of the base polymer so obtained, study the effect of thermal property of the base polymer, and measure the photosensitivity of this base copolymer.

3. To formulate a suitable composition of lithographic plate coating.

4. To study lithographic properties of the lithographic plates.

1.3 Scope of the Research Work.

In this research work, the focus is the synthesis of the copolymer of methyl methacrylate and methacrylic acid by radical polymerization. The necessary process to achieve the goal may be as follows.

1. Survey and in-depth study of the literature in this research work.
2. Design and prepare the experimental apparatus and chemicals.
3. Synthesize the copolymer of methyl methacrylate (MMA) and methacrylic acid (MAA) by radical polymerization by varying the following parameters.

  - The ratio of the monomers MMA:MAA
  - The reaction time
4. Characterize these copolymers by NMR and IR spectroscopic technique.
5. Investigate molecular weight and distribution by GPC and thermal behavior by DSC.
6. Mix the copolymers with the light sensitive composition and formulate the suitable composition for coating the Al plate.
7. Spin coating of the coating formulation on an Al plate to form a photosensitive film.
8. Coat the light sensitive layer with 2% poly(vinyl alcohol) (PVA) to prevent from oxygen and dry with a hair dryer.
9. Expose the coating to UV source by varying exposure time. They are then developed in an alkaline developer.
10. Evaluate the quality of lithographic plate by image analyzer and contact angle.
11. Observe the images that were printed from the lithographic plate.
12. Summarize the results and write up the thesis.

1.4 Contents of the Research Work.

This thesis consists of 5 chapters. The first chapter deals with the background, the interest and the scope of this research work. Chapter 2 provides the theory of photoresist technology, UV coating and related theory that are important for understanding. Additionally, it includes literature reviews of the previous works that give useful information and trends for work. Chapter 3 is the experimental part that describes about chemicals, equipment, apparatus, procedure for important parameters of reaction investigated in this work. The results and discussion are explained in Chapter 4. The effect of various reaction parameters and the effect of the exposure time on the quality of the lithographic plate are elucidated and discussed in detail. Finally, the summary and suggestion are in Chapter 5.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Free-Radical Polymerization [5, 6]

All free-radical polymerizations have at least three basic reaction types occurring simultaneously during polymerization. These include: initiation reactions which continuously generate radicals during the polymerization; propagation reactions which are responsible for the growth of polymer chains by monomer addition to a radical center; and bimolecular termination reactions between two radical centers which give a net consumption of radicals. Free-radical may be generated by the chemical decomposition of azo and peroxide compounds, thermally and by γ-radiation. The initiation step composes of two reactions including (a) the production of primary radicals (Equations 2.1a - 2.1b), the addition of primary radicals produced to the first monomer molecule to obtain the initiating species $M_1^{\bullet}$ (Equation 2.1b). The initiator (I) is usually homolytically dissociated to yield a pair of radicals $R^{\bullet}$

$$I \xrightarrow{\quad} 2R^{\bullet} \tag{2.1a}$$

where k_d is the rate constant for the initiator dissociation.

The second reaction of the initiation can be shown as follows:

$$R^{\bullet} + M \xrightarrow{\quad} M_1^{\bullet} \tag{2.1b}$$

where M is a monomer molecule and k_i is the rate constant for the initiation step.

The propagation step consists of the growth of $M_1^{\bullet}$ by the addition of large number of monomer molecules. Each addition creates a new radical which has the same identity as the one previously mentioned, except that it is larger by one additional monomer unit. This step can be presented in a general term as

$$M_n^{\bullet} + M \longrightarrow M_{n+1}^{\bullet} \qquad (2.2)$$

where k_p represents the propagation rate constant.

The growth of chain takes place very rapidly, the average lifetime of the growing chain is short, for instance, a chain of over 1,000 units can be produced within 10^{-2} to 10^{-3} sec. In theory, it could continuously propagate until all the monomers in the system had been consumed. If the radical concentration is high, the short chains are generally produced due to a high probability of radical interactions. The long chain polymer could be produced in the system having low radical concentration.

Termination of the growing chains may take place by the reaction of the radical center with initiator radicals; transfer of the radical center to another molecule (such as solvent, initiator or monomer) and interaction with impurities (such as oxygen) or inhibitors. The bimolecular reaction between two radical centers is the most important termination reaction. There are the combination which occurs by the coupling of two radical centers to form one long chain; and the disproportionation which a hydrogen atom in *beta* position of one radical center is abstracted by another radical center to give a saturated and unsaturated polymer chain. One or both reactions may be active in any system depending on the monomer and polymerizing condition. The general term expressing the termination step is

$$M_n^{\bullet} + M_m^{\bullet} \longrightarrow \text{dead polymer} \qquad (2.3)$$

where k_t is the combination of the rate constant for the termination step.

2.2 Photoresist Technology [7]

Photoresists are essentially systems where a layer of material sensitive to light is coated onto a surface and then exposed to actinic radiation generally in visible and near-UV regions of the electromagnetic spectrum through a master – image or pattern. This causes a solubility change of the layer. The more soluble parts can be removed on treating the layer with a solvent. This leaves an image – wise stencil of the support. (see Figure 2.1)

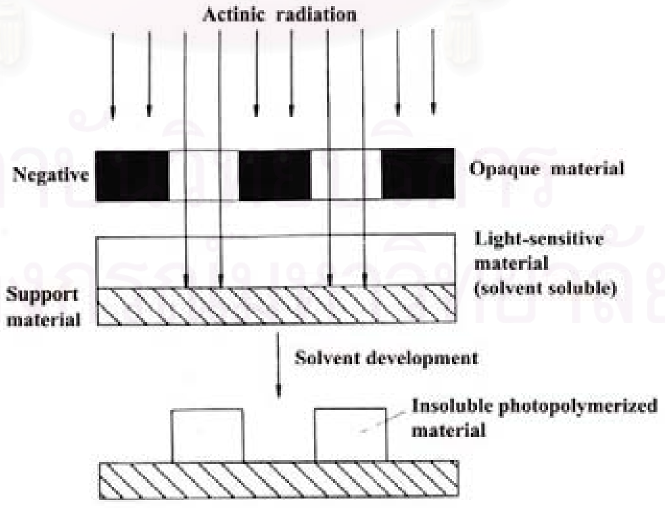


Figure 2.1 A typical photoresist [7].

The image formed may then perform as a resist, often against chemicals such as acid or alkali. Photoresists are often broadly categorized into two main types. These are negative working photoresists and positive working photoresists. They have three main components:

1. A photoresponsive compound is destroyed on exposure to actinic radiation.
2. An acidic polymer.
3. A solvent as an aqueous basic developer.

2.2.1 Classes of Systems Used for Photoresists [7]

There are many classes of systems used for photoresists. These include:

1. Crosslinking of a light-sensitive colloid or synthetic polymer by the addition of a photo-sensitizer that causes decomposition to form an active species that insolubilizes the surrounding vehicle or binder. For example, dichromate/gelatin or azide rubber.

2. Polymers containing photosensitive groups built in situ of the structure forming crosslinks between their molecules on exposure to actinic radiation, to significantly lower their solubility, such as poly(vinyl cinnamate).

3. Photopolymerization providing the means of insolubilization, whereby monomeric compounds are made to polymerize via actinic radiation with or without a photo-sensitizer/initiator present.

The desirable features for an acid/alkali photoresist include:

1. Good hydrophobic character
2. Rapid light sensitivity (minutes as opposed to hours)
3. Good solubility differential

2.2.2 Application of Photoresists [7]

Photoresists find applications for several printing processes. The major areas of interest include:

1. Printing plates
2. Photoengraving
3. Silkscreen printing
4. Printed circuits
5. Collotype
6. Proofing systems

2.3 Printing Plates [7, 2]

Photopolymerization by actinic radiation is used extensively in the preparation of printing plates

The kind of plates involved may be categorized into the following groups:

(a) Relief or raised image;

(b) Planographic, photolithography;

(c) Gravure or intaglio-photoengravure;

But photopolymerization is finding use primarily in (a) and (b)[7]. In this research we are concerned with photolithography and planographic plates.

All printing processes reproduce lines and dots that form the image. Printing is the process of manufacturing multiple copies of graphic images. Although most people think of printing as ink on paper, printing is not limited to any particular materials or inks. The embossing process uses no ink at all, and all shapes and sizes of metals, wood, and plastics are common receivers of printed messages.

The following four major printing processes are used to reproduce graphic images:

- Relief printing
- Intaligo printing
- Screen printing
- Lithographic printing

Each of these processes is suited for specific applications, such as newspaper, book, package, or textile printing.

In these research we study Lithography, as it is known today as a relatively new process, dating from around 1978. A lithographic image is transferred from a flat surface. Certain areas on the surface are chemically treated to accept ink, and other areas are left untreated so that they will repel ink. When the surface is inked, the ink remains in the ink-receptive areas, but not in the untreated areas. When the material such as paper contacts the surface, ink is transferred to the paper. This process is sometimes called planography, offset lithography, offset, or photo-offset lithography.

Offset lithography printing is the most widely used printing process in the commercial printing industry. Its major application is for printing on paper, thus it is ideal for printing newspaper, books, magazines, pamphlets, and all other forms of paper publications[2].

2.3.1 Lithographic Printing Plate [4, 8]

The conventional lithographic plate is required to present two different types of surface to the printing system. The first is a hydrophilic surface, receptive to the aqueous damping system of the printing press, in order to define the ink-rejecting (non-image) areas. The oleophilic (ink-receptive) image-forming areas of the plate are those provided by the photosensitive coating. The hydrophilic surface of the plate is usually of grained and anodized aluminium. The graining of plates was a process introduced to increase the surface area of porosity of the plate so that it could retain larger volumes of water, thus improving its ink repellency. The original graining process was a mechanical operation in which the surface of the aluminium plate was abraded by the prolonged action of ball bearing shaken across the plate surface on an oscillating table.

Although the oil repellency of metals is not great, their surface oxide layers are strongly hydrophilic, attracting water which in turn repels ink. Aluminium is a highly reactive metal that quickly forms an oxide layer in air. To enhance the hydrophilicity of the surface this oxide layer is removed and then replaced by chemically anodizing the surface using phosphoric acid. The result is a tough hydrophilic oxide layer having an extensive surface area capable of collecting relatively large volumes of water. The hydrophilic character of the layer is increased and protected from finger grease by coating with a hydrophilic colloid such as gum arabic which adsorbs onto the lithographic surfaces.

In modern graining and anodizing technology, the plate surface is roughened and anodized by electrochemical treatment of the metal. The resulting surface has a vastly increased area because the electrolytic process attacks minute sites in the crystalline structure of the aluminium sheet creating a microscopic network of channels in the surface. The capacity for holding water is thus hugely increased but the water is retained within the microstructure of the plate to a much greater extent than with conventional graining. This reduces the free surface water present on the plate and in turn reduces surface ink emulsification. Moreover, greater control of the surface characteristics of the plate gives higher resolution capabilities for fine half-tone dot reproduction [4].

Today the standard litho plate, used by printers in Europe, the US and Japan, is an UV-sensitive, aqueous-developed, grained and anodized aluminium plate, either negative or positive, which can run on any press. There are specialty plates aimed to the different segments, offering very smooth plates for fast ink uptake on small presses or very durable and water-receptive backgrounds to minimize scumming on the fastest web presses. However, the economics of production have led to the refinement of multipurpose litho plates that can operate across the market segments.

There are considerable regional differences in the types of plate and plate making methods used, but some things are fairly well universal (Table 2.1)

Table 2.1 Summary of applications [8].

Application	**Positive plates**	**Negative plates**	**Camera**
Monochrome text	×[a]	✓[a]	✓
Forms, cheques	×	✓	✓
Newspaper	×	✓	✓
Sheet-fed color	✓	✓	×
Color web	✓	✓	×
Packing	✓	×	×

[a] × = non-applicable, ✓ = applicable

The differences are most marked in the use of negative plates for quality, commercial color in the US market. In the rest of the world printers use positive plates for this application but the US values the clean working of negative film stripping greater than the transparency of operation and ease of text stripping into positive film assemblies, which are given by European and Japanese printers as their reason for using positive plates [8].

Central success to the litho process is the ability of the plate to separate the ink and water into discrete parcels for transfer to the press. This is achieved by having a large difference in oleophilicity and hydrophilicity between areas of image and non-image, which are almost coplanar on the plate.

Figure 2.2 gives us other insights. If the grain (that is the roughness of the plate) is too high then the coating has to be thicker to cover it. If the grain is too low, the smooth surface is less water receptive and there is more chance of ink catch-up, which makes the level of the water critical—too little and the plate catches up too much water and the plate is flooded.

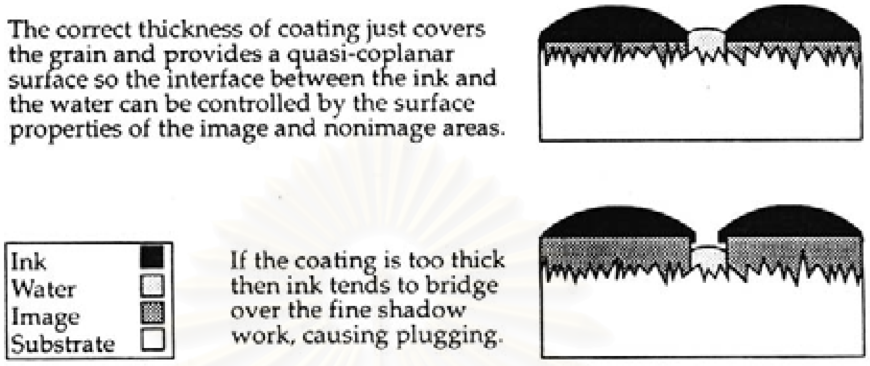


Figure 2.2 Aluminium litho plate [8].

The correct thickness of coating just covers the grain and provides a quasi-coplanar surface so the interface between the ink and the water can be controlled by the surface properties of the image and non-image areas.

Figure 2.2 illustrates the aluminium substrate, the most commonly used plate support, but the same principles may be applied to paper and plastic plates as well. In all cases, the background must be sufficiently water receptive to keep it clean from ink on the run, especially through stop-downs. Quantifying this property is difficult without a press, but a system developed by GraphoMetronic has gone as close as anyone by measuring the water concentration on the image area and the background. The water on the image is emulsified into the ink and by following the amount of water on the plate and in the ink, it is possible to build up a profile of the ink-water balance of the plate. Although there have been advances in plate construction to aid the setting of good printing conditions the lithographic printing process is still heavily reliant on skilled practice.

While the printing properties are considered predominantly in terms of physical properties, such as ink and water receptivity, durability and dimensional stability, the plate must first be imaged and this is where the chemical properties of the materials become important. It must be possible to expose the coatings on practical exposure systems such as cameras for direct-to-plate or step-to-repeat machines for applications such as packaging and this leads to a multiplicity of photochemical solutions, together with a wide variety of techniques to expose them.

There are three substrates in general use for litho plates in the world today: paper, plastic and metal; as shown in Table 2.2 Invariably, these types can be further refined. However, the most versatile metal used for the plate support is aluminum.

Table 2.2 The substrates [8].

Substrate	Definition
Paper	0.100-0.175 mm paper coated both sides with a ‘waterproof’ polyethylene (PE) layer
Plastic	0.1-0.3 mm poly(ethylene terephthalate) (PET)
Metal	0.1-0.5 mm aluminium

2.3.2 Photopolymer Plates [3,4]

Polymers and plastics form an extremely important class of materials, which enjoy common applications in everyday life as well as in printing materials[3].

Photopolymer plates in general rely on the chemical polymerization of monomers or the cross-linking reaction of unsaturated long-chain polymers or prepolymers under the influence of ultraviolet radiation. The desired result is a solubility differential between the exposed areas and unexposed areas of the printing plate.

The requirements for photosensitive systems for printing plates are that they should respond to a reasonable exposure time, that the exposure should induce some useful change such as one of solubility and that, for lithographic plates, the image areas must be oleophilic or easily made so[4].

2.3.2.1 Negative and Positive Working Plates

Negative and positive working plates for lithographic printing differ in the chemistries of their light-sensitive coatings.

2.3.2.1.1 Negative Working Plate

In the negative working system, ultraviolet light causes the photopolymer coating to cross-link and harden. The plate coating is exposed through a photographic negative(screened in the case of half-tone images), and the clear areas on the negative transmit UV radiation to the reactive surface coating of the plate. The dark areas on the negative represent those reflecting light in the original, that is the screened mid-tone and highlight areas(white), whereas the clear regions correspond to darker or shadow tones. For black text on white paper, the negative produced would comprise dark areas corresponding to the white paper, and clear areas corresponding to the text. When printed down onto the negative working plate surface, UV radiation passes through the clear, (text) areas producing a light-hardened ink-receptive image of the text on the printing plate (the contrast or gamma of graphic arts lith film is very high, 14 or more. Hence light from original copy is only recorded above a specific intensity threshold, resulting in either a black silver image or clear film.)

The coating applied to negative working plates fall into three categories, defined by their action:

- Photoinsolubilization
- Photopolymerization
- Photocrosslinking

In all three processes, a solubility differential is set up between the exposed and unexposed areas of the coating, and the plate is developed using water, aqueous alkali or solvent. Environmental requirements have lead to great interest in aqueous developers.

2.3.3.1.2 Positive Working Plate

The positive working plate operates in the opposite manner in that a transparent film positive is used to make the exposure. In a film positive the tonal values of the original and the film are in the same sense. The clear areas on the positive therefore represent light tones in the original and vice versa. A requirement of the plate coating for positive working is that it should not form image areas where light passes through the film. Indeed, the coating must become solvent soluble in the exposed areas, the unexposed image areas remaining hard and ink receptive [4]. (see Figure 2.3)

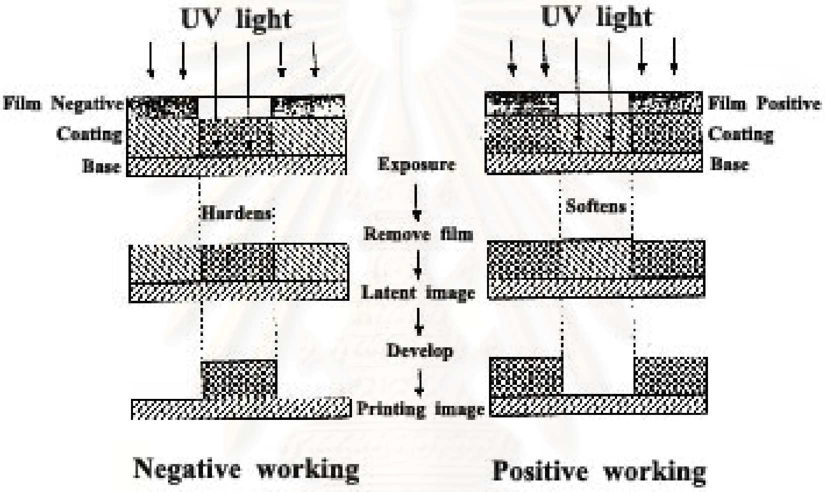


Figure 2.3 Exposure of negative and positive working plates [4].

2.4 Control of Platemaking [9,10]

The lithographic process is unique in being able to take advantage of many plate types and imaging methods. Plates may be imaged from reflection copy, by projection or contact, and imaging from digital data is now a reality and may become the norm in the future. At present, however, almost all process color printing employs surface presensitized plates, imaged from film contact exposure. Film positives are used for newspaper color and some packaging [9].

2.4.1 Platemaking – Basic Objectives [9]

When making a litho plates, we have to ensure some basic objectives, which are summarized below:

- Images should be correctly and accurately positioned relative to other images and plate itself.
- Imaging and processing should ensure and enhance the difference in wetting between image and non-image areas.
- Nonprinting areas should be well desensitized and free from marks and unwanted image.
- Ensure that maximum plate life is possible.

All of these properties relate to the functionality of the plate in the litho process, but it is apparent that the control of dot gain in printing is intricately tied to the control of image transfer in platemaking. Fortunately, modern presensitized plates are quality controlled during manufacture and imaging is relatively easy to control with the aid of some simple control devices.

2.4.1 Variables Affecting Image Transfer

The basic objectives to which we have referred are to a large extent satisfied by controlling exposure and by correct operation of the processing. This is also other important factors which must be considered.

2.4.2.1 Quality of Film Image

An important requirement of all films for platemaking concerns the clear film and image density. The image should have a minimum density of 2.4 and the base film should ideally have a density of not more than 0.05. An additional important requirement for halftone films relates to the definition of dots and absence of a significant fringe. Halftone films may frequently be referred to as first or second generation, or alternatively soft or hard. The first generation dots will normally have a fringe which is of a lower density than the core of the dot, whereas hard dot or second generation film will have a more uniform density. This difference is illustrated in Figure 2.4.

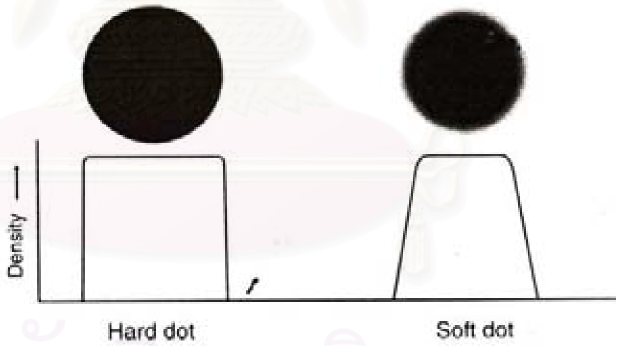


Figure 2.4 Characteristics of hard- and soft-fringed halftone dots [9].

These terms had particular relevance when halftones were produced using contact screens, but are less relevant with modern digital output devices where halftone dots are generated electrically. Nevertheless, some output devices produce dots with a fringe, and others may produce unsatisfactorily formed dots due to incorrect settings or processing.

The size of a dot transferred to a plate from a fringed dot can vary considerably as a result of only small changes in exposure (see Figure 2.5). These exposure variations can easily occur over the area of the printing down frame, due to poor uniformity of light coverage. It is not uncommon to find a 2-1 difference, between the center and edge of the frame. The problems with fringed dots can be made even more acute if the plate coating has a low photographic contrast (i.e. many grey steps reproduced when exposed to a continuous tone wedge).

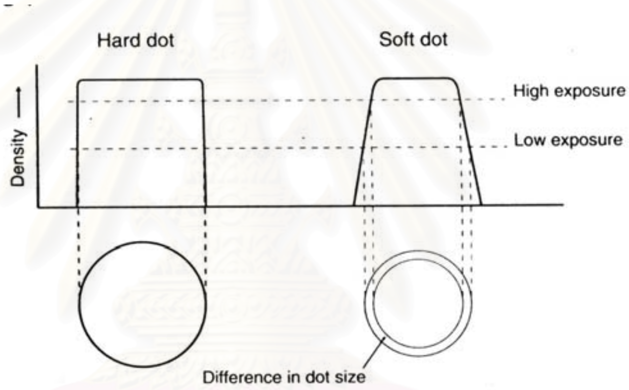


Figure 2.5 Effect of small exposure changes on dot size when making plates from fringed dots [9].

The film image for plate making should be free from any significant fringe. This can be assured through contacting to produce ‘final film’. Final films should therefore be specified for all plate makings.

2.4.2.2 Film Contact to Plate

Image loss or sharpening will result from poor contrast between film and plate when using positive working plates, and the reverse is true with negative plates. This may occur overall if the vacuum is insufficient, or in isolated areas due to poor stripping or where dirt is present. Even with good contact, light will inevitably undercut the area protected by the film image, but it is significantly greater if contact with the plate’s surface.

Modern printing down frames may attain vacuum very rapidly, which makes it easy for air to become entrapped. For this reason it is important to make use of two stages of vacuum, where the frame allows for this. The first stage should be just long enough to raise the plate and film up, to make enough pressure to ensure complete evacuation of the air. It is tempting to reduce this time in order to speed up the process, but this should be avoided.

Plate manufacturers have made developments to reduce the possibility of air entrapment by modifying the coating surface to allow the air to leak away more easily. It may be noticed, therefore, that contact problems are more acute with one manufacturer’s plates than another.

Isolated areas of poor contact may occur if care has not been taken with the stripping or cutting of film. It may also be noticed that this affects thicker plates more significantly, as they have more difficulty in distorting to accommodate the different thickness layers of film (see Figure 2.6). Dust and dirt are also a major problem with respect to contact and it is important that the plate making area is kept as clean and dust-free as possible. It is particularly noticeable on microline and small dot patches, and usually results in unpredictable transfer of these lines or dots.

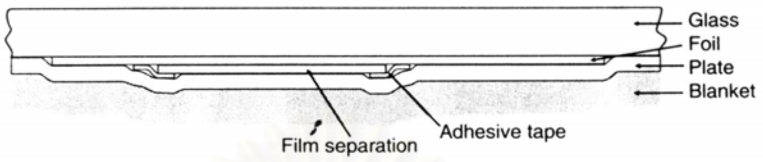


Figure 2.6 Cross-section view to illustrate how the plate has to distort in order to obtain good contact [9].

2.4.2.3 Use of Diffusion Foils

Plate exposure is typically achieved using a metal halide light source, which is housed in a reflector designed to provide as near uniform exposure over the full area of the plate as possible. The angle at which light falls on the plate and the refraction of light passing through the film positive cause shadows to be cast at the edges of film and tape. Such shadows produce unwanted images on the plate, which have to be deleted with correction fluid or exposed with a burnout exposure.

The shadows can be reduced by applying all or part of the exposure through a diffusion foil. While this reduces the film edge marks it also increases the amount of undercutting of the image. The extent of undercutting can be unpredictable and is dramatically increased if there are areas of poor contact. For this reason it is not a recommended practice where accurate transfer of halftone images is to be achieved, particularly if the screen ruling is extremely fine.

2.4.2.4 Plate Resolution

Plates from different manufacturers may have different resolving power, particularly where there is a marked difference in graining or image coating. The differences are not so great as to limit a plate’s use for normal halftone reproduction, but a knowledge of the plate’s resolving power is desirable in order to correctly determine standard exposures.

2.4.2.5 Exposure

The amount of light to which the plate is exposed is the principal variable that the platemaker has to adjust in order to control the image transfer to plate. It is also the most significant factor affecting the basic plate requirements that has been explained at the beginning. All plates need a sufficient level of exposure in order to make the required change take place in the coating, so that a proper differential between image and non-image is achieved and an acceptable plate life is achieved.

Increased exposure reduces image sizes on positive working plates and increases it on negative plates. The correct exposure time for a plate has to be established by the platemaker since it is affected by:

- speed and sensitivity of the plate coating,
- spectral output of the exposing light source,

- distance of light source from the plate,
- density of film and foils.

The intensity of actinic light will reduce during the life of the plate exposure lamp and may vary with fluctuation in the power supply. For this reason control of the exposure is greatly improved if its duration is measured by a light integrator rather than a timer. Since we are only concerned with the actinic light to which the plate is sensitive, the integrator should therefore be filtered to provide this sensitivity.

With some poorly designed exposure units there may be considerable variation in the intensity of actinic light from the outer edge of a plate. This is estimated to be as great as 2 to 1 in some instances. The significance of these differences in terms of controlling image transfer will depend on the film and exposure latitude of the plate being used.

A different type or batch of plate may necessitate different exposure setting to achieve a standard image transfer. It should therefore be normal practice to check each new batch of plates to establish if any change is necessary.

2.4.2.6 Processing

Most presensitized plates allow considerable latitude when developed and variations on image transfer caused by processing are not normally significant. It is important to stress, however, that the developer should be kept at a temperature above 16 °C and not allowed to become exhausted, as this will retard the development of the plate.

2.4.2.7 Measurement with a Densitometer

Although claims are made that the densitometer can be used to provide dot area measurements on the plate, the resulting values are not accurate or reliable, nor is it convenient as a matter of regular routine to use the densitometer to measure plates. Plate image control is therefore achieved with the aid of plate control strips[9].

2.4.3 Plate Control Elements [9]

There are a number of control elements available that are useful to the platemaker. These may take the form of specific targets used to establish exposure conditions for plates and other similar materials. Such elements are normally too large to be included on all plates, but may be exposed in the nonprinting, clamped area of the plate. Other elements may be incorporated into a print control strip, which intended to appear on the printed sheet. There are a number of manufacturers producing similar elements, but the UGRA Plate Control Wedge (PCW) contains most of the important elements. This will therefore be referred to when describing the various types of element[9].

UGRA-Plate Control Wedge [10]

The UGRA plate control wedge (see Figure 2.7) is intended for controlling the platemaking process in lithography. Futhermore, it is possible to use the PCW for some evaluations in the proofing process and for printing tests.

On the printing plate the following criteria can be evaluated:

- Exposure
- Exposure latitude
- Optimum resolution
- Gradation
- Rendering of halftone dots

When making proofs and production prints it is possible to assess:

- Slur and doubling
- Tone reproduction

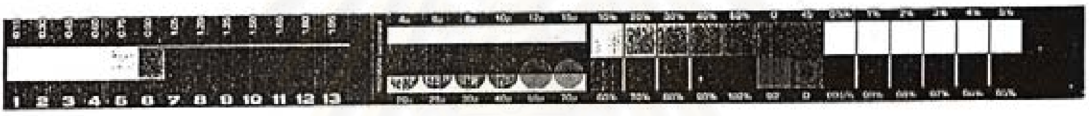


Figure 2.7 UGRA plate control wedge (PCW) [10].

The UGRA PCW is made from two different films, a high-resolution line film and continuous-tone film. The latter, consisting of 13 continuous-tone steps, is stripped into a window of the line film with an adhesive tape.

2.5.3.1 Continuous-tone Wedge

(See Figure 2.8)

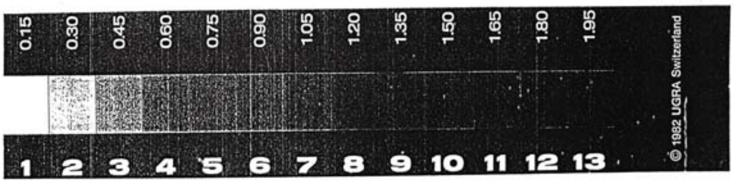


Figure 2.8 Continuous-tone wedge [10].

2.5.3.1.1 Density Values

The density values are labelled on top of the continuous-tone patches. These values are correct for a densitometer that is zeroed without film base.

Tolerances

- deviation from the specified density value: ± 0.02
- difference between two steps: 0.15 ± 0.02

2.4.3.1.2 Relation between Exposure Time and Rendering of the Continuous-tone Wedge

For a given type of light sensitive materials, the continuous-tone wedge indicates differences in exposure according to the following rules (see Table 2.3). This rule holds for any continuous-tone wedge having a step increment of 0.15.

Table 2.3 Continuous-tone wedge [10].

If two tests show a difference in the wedge of:	There is a difference in exposure by the factor:
1 step	1.4
2 steps	2
3 steps	2.8
4 steps	4
5 steps	5.6
6 steps	8
7 steps	11

If a higher step of the continuous-tone wedge should print on the plate, the initial exposure time has to be multiplied with the above indicated factor. If a lower step is desired, the initial exposure time must be divided by the factor.

Example: To proceed from step 5 to step 7, the exposure time should be doubled.

To go back from step 4 to step 3, the exposure time must be divided by 1.4.

2.4.3.1.3 Control of Exposure

The correct exposure cannot be determined from the continuous-tone wedge alone. It is necessary to make a series of exposure and evaluate the reproduction of micro-lines. Once the correct exposure for a certain plate has been determined, it then can be maintained by keeping the reproduced continuous-tone step constant

In general, optimum exposure is applied, when the first printing step in the continuous-tone wedge for the different light-sensitive coatings is as follows:

Diazo coatings (positive working): step 4 to 5
Diazo coatings (negative working): step 3 to 5
Photopolymers: step 3 to 5

These specifications refer to the reproduction of the continuous-tone wedge after developing. If the light-sensitive coating is removed (e.g. in multimetal platemaking), then the evaluation of the continuous-tone wedge on the finished plate becomes meaningless.

2.4.3.1.4 Evaluation of Gradation

The gradation of a light-sensitive coating can be judged by counting the number of continuous-tone steps that are neither fully solid nor fully non-printing.

The following values are typical for the different light-sensitive coatings:

Diazo coatings (positive working): 4 to 7 steps
Diazo coatings (negative working): 4 to 7 steps
Photopolymers: 1 to 2 steps

Again, these specifications refer to the light-sensitive coating after developing.

2.4.3.2 Micro-lines

(See Figure 2.9)

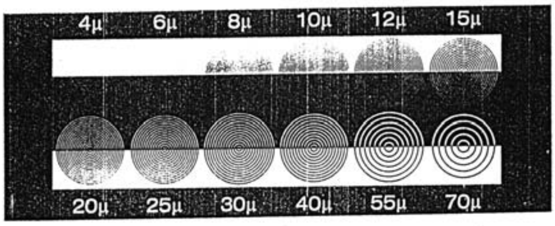


Figure 2.9 Micro-line [10].

2.4.3.2.1 Specifications

The 12 patches of micro-lines have the following value (see Table 2.4):

Table 2.4 The values of the 12 patches of micro-lines [10].

Width (μm)	**Distance (μm)**	**Area covered (%)**	**lines/cm**
4	36	10	250
6	54	10	167
8	72	10	125
10	90	10	100
12	108	10	83
15	135	10	67
20	120	14.3	71
25	135	15.6	62
30	150	16.6	56
40	200	16.6	42
55	275	16.6	30
70	300	16.6	24

The micro-line patches of the UGRA PCW have the same values as the micro-line patches in the FOGRA-PMS-K-patch. (Compared with the K-patch in the FORGRA-PMS Color Control Bar, the UGRA PCW has additional line widths of 4, 25, 40, 55 and 70 microns.) Therefore, the micro-lines of the UGRA PCW can be evaluated according to the same guidelines as the ones established for the FORGRA-K-patch.

2.4.3.2.2 Determination of Optimum Resolution

In order to determine the optimum resolution of a plate (or film), a series of exposures is made such that each following exposure time is the double of the preceding one.

Example for a series of five exposures:

20 – 40 – 80 – 160 – 320 sec

The aim is now to find the exposure time at which the positive and negative lines are lost simultaneously at the same line with (see Figure 2.10). The optimum resolution is then specified as the line width of the lowest step where positive and negative lines are still just visible. A line patch is considered to be reduced to zero or to be a solid-tone, if less than a third of the line is left.

The determination of the optimum resolution has to be made on the finished plate, i.e. on multimetal plates after etching.

The optimum resolution of direct printing plates ranges from 4 to 8 microns, mostly being about 5 to 6 microns. This is valid for diazo coatings and photopolymers. Multimetal plates have an optimum resolution from 9 to 14 microns, and this is independent of which light-sensitive coating is used.

The exposure time to achieve the optimum resolution is not significantly different for the different light-sensitive coatings. Dependent on the coating thickness the exposure time can vary up to a factor 4 for the same type of coating.

Figure 2.10 Determination of optimum resolution: Within a series of exposures that patch is located where the positive and negative lines are almost simultaneously at the same patch. In this example, the optimum resolution is 10 µm [10].

2.4.3.2.3 Determination of Exposure Latitude

The exposure to achieve the optimum resolution can be considered as the minimum required exposure. A further increase of exposure results in an undercutting by light yielding a dot loss on positive working plates and a dot gain on negative working plates. Thus, exposure latitude can be defined as the difference between the minimum required exposure and the exposure at which undercutting does not exceed a certain degree. In this manual, exposure latitude is defined as the range where the degree of undercutting does not exceed 5 microns.

Starting from the exposure time to achieve the optimum resolution, the exposure time is determined where the width of the positive lines being reduced to zero has increased by 5 microns. (This applies for positive working plates. On negative plates, the width of the negative lines being turned to solid-tone has to be judged.)

For positive working diazo plates the upper limit of the exposure latitude is mostly two to five times higher than the exposure to achieve the optimum resolution.

2.4.3.3 Halftone Wedge 60 lines/cm

(See Figure 2.11)

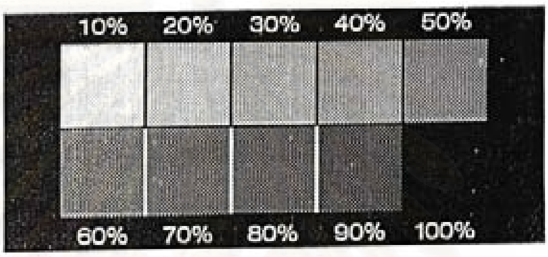


Figure 2.11 Halftone wedge 60 lines/cm [10].

2.4.3.3.1 Shape of the Halftone Dots

The shape of the dots was calculated and plotted using the FOGRA chain dot model. (In order to use a standard half-tone dot model, UGRA refrained from using its own model.) A moderate chain dot shape was chosen according to the current knowledge about the ideal dot shape. The dot areas where corner link-up takes place are symmetrical to 50%:

First corner link-up: 42.5 %

Second corner link-up: 57.5 %

The screen angle is 45 °

2.4.3.3.2 Relationship Between Dot Area and Dot Diameter

The important advantage of plotted halftone dots is that there is a known mathematical relationship between dot area and dot diameter. Based on dimensional measurements it is possible to draw conclusions as to changes in the tonal values. (When halftone dots are printed on paper the diffusion of light has to be also considered.)

The diameter values (in micron) are shown in Table 2.5:

Table 2.5 The diameter values [10].

Step(%)	Horizontal[*]	Vertical	Diagonal
10/90	61	59	58
20/80	91	84	81
30/70	118	105	96
40/60	149	128	107
50	167[**]	149	118

[*] horizontal relative to the screen direction.

[**] not measurable because of the corner link-up, the value is identical with the length of one side of unit area

The dot areas of the steps of 40%, 50% and 60% deviate not more than 1 % from the labelled values.

2.4.3.3.3 Application of the Halftone Wedge

The purpose of the halftone wedge is to evaluate tone reproduction. As far as routine control of platemaking is concerned, micro-lines and continuous-tone wedge are better suited tools than halftone dots.

The steps of the halftone wedge have been chosen such that sufficient measuring points are available to plot a characteristic curve of the printing process. As the dot areas are multiples of 10%, calculation and plotting of dot gain values is facilitated.

On printing plates, only dimensional measurements are meaningful, since densitometric measurements do not provide exact values.

The halftone steps of 40%, 50%, 70% and 80% permit evaluation of dot gain in comparison with commercially available color control strips. The above-mentioned dot areas exist in the following color control strips (see Table 2.6)

Table 2.6 The color control strips [10].

Control Strip	**40%**	**50%**	**70%**	**80%**
Brunner		×		
FOGRAPMS	×			×
GRETAG CMS-1			×	
GRETAG CMS-2	×			×

However, that the dot shape in the above-mentioned color control strips does not correspond with the dot shape of the UGRA PCW.

2.4.3.4 Standardisation of the Platemaking Process

Although the exposure time required to achieve the optimum resolution and the exposure latitude are objective criteria, the “correct” exposure time can not be directly derived from it.

The exposure time to achieve the optimum resolution can be considered as the minimum required exposure. If this exposure time is exceeded, the positive halftone dots become smaller which may not be desirable. Simultaneously the negative halftone dots become more open which is usually desired. Also, film edges are reduced with increasing exposure time.

Hence, the "correct" exposure time is a compromise. Depending on the image, it may be desiderable that

- the shadows are sufficiently open
- the highlights are not too much undercut
- the film edges are eliminated to an extent that only few corrections on the plate are necessary.

So, since there are no objective criteria for the "correct" exposure time, it is reasonable to define an arbitary criterion in order to standardise the platemaking process.

Recommendation for a standardised platemaking process " The exposure time has to be chosen in such a way that the last reproduced patch of micro-lines is 4 microns above the optimum resolution." The reproduction of the micro-lines must be judged on the finished plate, i.e. on multimetal plates, after etching.

Investigations of UGRA and FOGRA showed that, if a positive working plate is exposed at 4 microns above the optimum resolution, the dot area of halftone dots in the middle-tones is reduced by 2 to 4 %. On negative working plates the dot area increases by about 3 to 5 %.

2.4.3.5 Application of the UGRA-PCW on Negative Working Plates

In contrast to positive working plates, on negative plates the dot areas of all image elements increase with increasing exposure time.

Table 2.7 Difference between positive and negative working plates [10].

	Effects of increasing exposure on:	
	Negative working plate	**Positive working plate**
Positive lines and dots on plate become	Larger	Smaller
Negative lines and dots on plate become	Narrower	Wider

The design the UGRA PCW is such that suited equally well for positive and negative working plates. Micro-lines and the continuous-tone wedge can be applied without regard as to the type of plate. However, the labels on the halftone scales, are no longer correct. (The correct values are obtained by subtracting the label values from 100%).

When printing the slur target from a negative plate, the dot area is 40% rather than 60%. This causes a somewhat smaller sensitivity. Therefore density measurements from negative working plates should not be compared with measurements from positive working plates[10].

2.5 Rheology [11]

Rheology is the study of the flow and deformation of matter. The aim of this science is to define and evaluate such words as consistency, tack length of flow, stiffness and body in terms of the physical properties of the material.

2.5.1 Flow in Ideal System

Isaac Newton was the first to find the basic law of viscometry describing the flow behaviour of an ideal liquid.

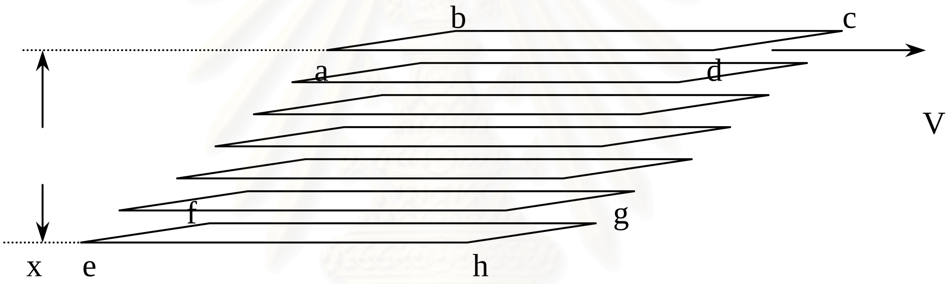


Figure 2.12 Newtonian flow [11].

Considering two parallel planes, abcd and efgh of area A (Figure 2.3) in a fluid, holding efgh stationary and subjecting abcd to a force F resulting in a movement of velocity V, the intervening fluid may be looked upon as having many planes sliding over one another. The nearer the planes are to plane abcd, the greater is their velocity. Consequently, there is a velocity gradient between the planes abcd and efgh:

$$velocity\ gradient = \frac{dV}{dX} = D\,(rate\ of\ shear)\,(s^{-1}) \qquad (2.4)$$

the shearing stress is given by the force per unit area

$$\tau = \frac{F}{A} \tag{2.5}$$

For a newtonian liquid τ is proportional to *D*, i.e.

$$\tau = \eta D \tag{2.6}$$

where η is a constant for the liquid under examination and is known as the coefficiency of viscosity. The unit of viscosity is the pascal second and is derived as follows:

$$\mathit{Shearing\ stress} = \mathit{force\ per\ unit\ area} = \mathit{newton}\ m^{-2} = \mathit{pascal} \tag{2.7}$$

$$\mathit{Shear\ rate},\ D = \mathit{velocity\ gradient} = \frac{dV}{dX} = \frac{m\,s^{-1}}{m} = s^{-1} \tag{2.8}$$

$$\mathit{Coeffiiency\ of\ viscosity} = \frac{\tau}{D} = \frac{\mathit{newton}\ s}{m^{2}} = \mathit{pascal}\ s \tag{2.9}$$

2.5.2 Newtonian [11]

These fluids have the same viscosity at different shear rates. The flow curve for an ideal liquid is a straight line, the ratio of all pairs of τ and D values belonging to this line is a constant. This means that η is not affected by changes of shear. All liquids for which this statement is true are called “Newtonian”.

The flow and viscosity curves of a Newtonian fluid are shown in Figures 2.13 and 2.14, respectively.

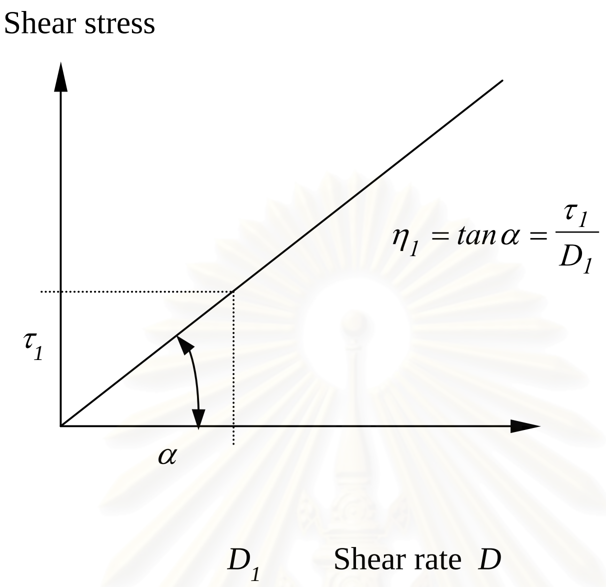


Figure 2.13 Flow curve of a newtonian liquid [11].

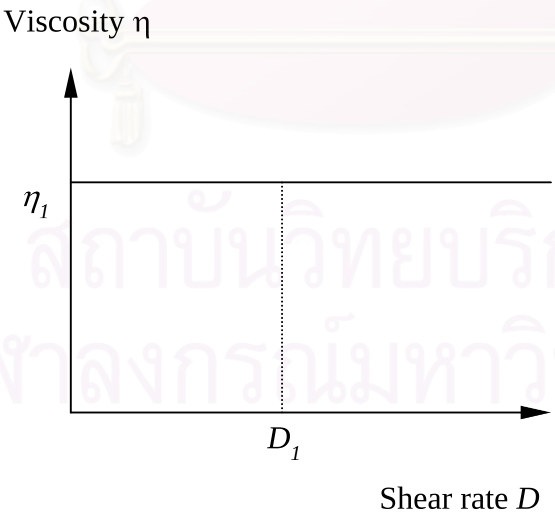


Figure 2.14 Viscosity curve of a newtonian liquid [11].

2.5.3 Non-Newtonian Liquid [12, 13]

All other liquids not showing this simple “ideal” flow behavior are called “Non- Newtonian”. From the flow curves thus obtained, it is found that the behavior of viscous liquids can be classified into five categories, shown diagrammatically in Figure 2.15

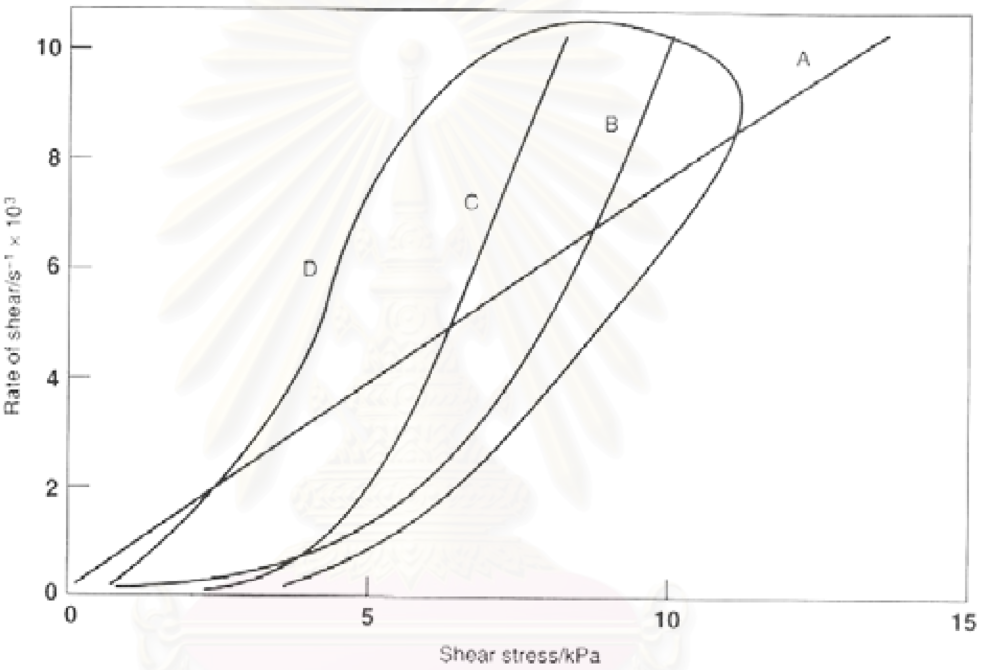


Figure 2.15 Typical flow curves demonstrating behaviour of viscous liquid [12].

A few materials, such as gum arabic paste, poly(vinyl alcohol) solutions and silicone oils, are essentially Newtonian (curve A in Figure 2.15), with viscosity independent of shear. Most print pastes show that is also known as pseudoplastic behavior or shear thinning properties, (curve B in Figure 2.15), with a significant reduction in apparent viscosity as the shearing stress is increased. The change is reversible, the viscosity increases immediately, shearing is then reduced. A significant number of pastes do not flow at all until the shear stress exceeds a minimum value, known as the yield value (curve C in Figure 2.15). Beyond this value, they may show either linear or nonlinear flow properties. The former has been called Bingham systems, after E. C. Bingham, who defined the term “plastic viscosity” as the ratio (shear stress-yield value): rate of shear. The concept of plastic viscosity has been extended to shear-thinning print pastes, with flow curves that approach linearity at high shear, by extrapolating the linear section of the curve back to the stress axis to define a yield value.

A great number of substances such as emulsions, suspensions, or dispersions of high technical and commercial importance are included in pseudoplasticity. It will be worthwhile to indicate some reasons for the shear thinning effect of pseudoplastic material.

Many liquid products that seem homogeneous throughout are in fact composed of several ingredients: particles of irregular shape of droplets of one liquid are dispersed in another liquid [13]. On the other hand there are polymer solutions with long entangled and looping molecular chains. At rest all of these materials will maintain an irregular internal resistance against flow, i.e. a high viscosity.

With increasing shear rates matchstick-like particles suspended in the liquid will be turned lengthwise into the direction of the flow. Chain-type molecules in a melt or in a solution can disentangle, stretch, and orient parallel to the driving force. Particle or molecular alignments allow particles and molecules to slip pass each other more easily and this shows up as reduced viscosity.

For most liquid materials, the shear thinning effect is reversible, often with some time lag, that is the liquids regain their original high viscosity when the shearing is slowed down or is even terminated: the chain-type molecules return to their natural state of non orientation, deformed droplets return to ball-shape and the aggregates reform due to Brownian motion

A fourth type of behavior, found in pastes with high pigment concentrations, has been called dilatant, but is better described as “shear thickening” to avoid the assumption that volume expansion necessarily occurs. This is the phenomenon seen on wet sand when pressure causes particles to touch and the friction between particles prevents their movement into expanded spaces. Free liquid is drawn into these spaces, making the system look dry.

Finally, there is the phenomenon known as thixotropy, shown by gelatin solutions and betonite suspension, for example (curve D in Figure 2.15). In this case the measured values of viscosity depend on the duration of shear as well as the rate of shear, and increased resistance to shear is observed after a long rest time than after a shorter time. The probable explanation is that intermolecular bonds are broken by shear and slowly reformed after shearing ceases.

2.6 Printability of the Printing Plate

From the lithographic plate, a lithographic image is transferred from a flat surface. Certain areas on the surface are chemically treated to accept ink, and other areas are left untreated so that they will repel ink. When the surface is inked, the ink remains in the ink-receptive areas, but not in the untreated areas. When the material such as paper contacts the surface, ink is transferred to the paper[2]. So the difference of hydrophilic/oleophilic property between image and non-image area is very important for printing quality.

The first step in obtaining good adhesion and print quality is to assure that image area can accept ink(oleophilic) and the non-image area can receive water(hydrophilic). As a result, the more interfacial area between the liquid and substrate, the greater the possibility of achieving sufficient bonding.

2.6.1 Surface Tension and Surface Free Energy

Considering a drop of a one component liquid in equilibrium with its vapour and in the absence of an external force. The drop spontaneously assumes the form of a sphere, the shape which corresponds to the minimum surface to volume ratio. It can therefore be inferred that work must be done on the drop to increase its surface area, and hence that the surface molecules are in a state of higher free energy than those in the bulk liquid. This is in part explained by the fact that surface molecules have fewer nearest neighbours and, as a consequence, fewer intermolecular interactions than bulk molecules. There is then, a free energy change associated with the isothermal, reversible formation of a liquid surface and this is termed the surface free energy or, more correctly, the excess surface free energy. The terms are often used to mean specific (i.e. per unit area) surface free energy, the units of which are mJ m^{-2}. It must be emphasized that this surface free energy is not the total free energy of the surface molecules but the excess free energy, which the molecules posses by virtue of their being in the surface [14].

Surface Tension of liquid is a phenomenon that directly results from intermolecular forces between molecules of liquids. In other words, molecules at the surface of a drop of liquid experience a net force that draws them to the interior, which creates a tension in the liquid surface [15].

The force of tension is tangential to the surface of liquid. The surface tension units of measurement are:

$$Force\,/\,length = \frac{mN}{m} = \frac{dyne}{cm} \tag{2.10}$$

The symbol used here will be γ.

The surface energy of a solid defines molecular forces of its interaction with other surface. It is measured as free energy per unit area:

$$Energy\,/\,area = force\,/\,length = \frac{mJ}{m^2} = \frac{mN}{m} = \frac{dyne}{cm} \tag{2.11}$$

2.6.2 Surface Energetics and Contact Angle

There are no direct, reliable methods for determining surface energy or surface tension of solids. However, there are two main indirect methods of solid surface measurement, that is contact angle and inverse gas chromatography methods. In this thesis, contact angle measurement will be discussed, it is probably the most common method of solid surface tension measurement. Contact angle data, especially in the case of polymeric material, can be obtained with low price instruments and with simple techniques.

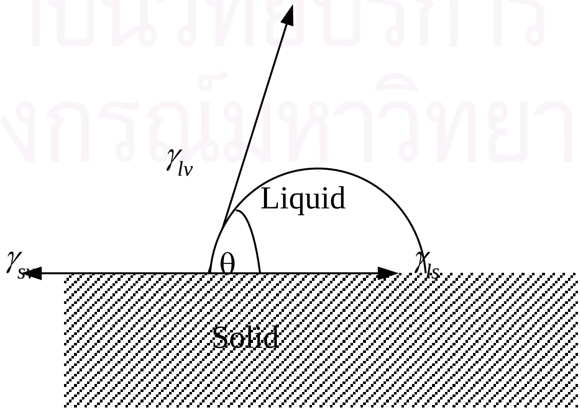


Figure 2.16 The Young equation [16].

At the basis of the measurement of solid surface tension by contact angle, there is the equilibrium at the three-phase boundary, shown in Figure 2.16 [16]. The drop of liquid that is put on a solid surface will modify its shape under the pressure of the different surface interfacial tensions, until reaching an equilibrium. In 1805, Thomas Young described the three-phase equilibrium in terms of the vectorial seem as shown in Figure 2.12 resulting in the following equation of interfacial equilibrium.

$$\gamma_{v} - \gamma_{sl} = \gamma_{lv} \cos\theta \qquad (2.12)$$

where γ_{ij} is the interfacial tension between phases *i* and *j*, subscripts *s*, *l* and *v* refer to solid, liquid and vapour, respectively; and θ is the equilibrium contact angle. The solid-vapour interfacial tension is linked to the intrinsic solid surface tension, or the surface tension of the solid in equilibrium with its own vapour or in vacuum, by the following relationship:

$$\pi_{e} = \gamma_{s} - \gamma_{sv} \qquad (2.13)$$

and π_e is called the spreading pressure, which represents the decrease of solid surface tension due to vapour adsorption. Equation 2.13 shows that, if π_e is negligible, the role of the spreading pressure will increase, for a given liquid, with increasing solid surface tension. It is generally accepted that if the contact angle is larger than about 10°, the spreading pressure can be safely neglected.

Equilibrium contact angle is obtained only on an ideal solid surface. An ideal solid surface is a perfectly smooth, chemically homogeneous, rigid, insoluble, and nonreactive surface.

2.6.3 The Actual and Apparent Contact Angles [17]

When real surfaces are considered, one should distinguish between two additional definitions of contact angles: the actual and the apparent. The actual contact angle (Figure. 2.17) is the angle between the direction of the tangent to the solid-liquid interface at that point. The usual optical methods for measuring contact angles yield the apparent contact angle (Figure. 2.18). This is the angle between the direction of the tangent to the seemingly smooth solid surface, as seen by using relatively low magnification, and the direction of the tangent to the lf interface. On perfectly smooth solid surfaces, the apparent contact angle is identical with the actual one. On rough surfaces, they may be very different.

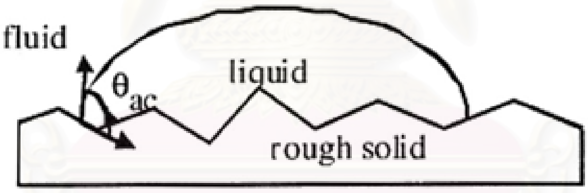


Figure 2.17 The actual contact angle [17].

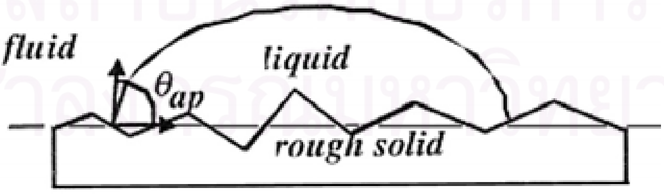


Figure 2.18 The apparent contact angle [17].

2.6.4 Contact Angle Hysteresis

2.6.4.1 Effect of Roughness [18]

In 1936, Wenzel reasoned that within a measured unit area of a rough surface there is more surface than in the same measured unit area on a smooth surface. While specific surface quantities are, the same on the two surfaces, the relative magnitude of the vectors composing the Young equation are modified, as shown in Figure 2.16. Wenzel proposed the following equation:

$$r(\tau_s - \gamma_{sl}) = \gamma_{lv} \cos\theta_w \tag{2.14}$$

where r is the so-called roughness factor:

$$r = actual\ surface/geometric\ surface \tag{2.15}$$

as illustrated in Figure 2.19. The subscript "*w*" indicated that the angle appearing in Equation 2.14, usually called the Wenzel angle, is different from that of the Young equation (Young angle, or θ_y). Their relationship is the following:

$$\cos\theta_w = r \cos\theta_y \tag{2.16}$$

Since the roughness factor is always greater than unity, Equation 2.16 shows that the effect of roughness is to magnify the wetting properties of the solid, that is the Wenzel angle will increase with roughness if the Young angle is greater than 90° and will decrease if it is less than 90°.

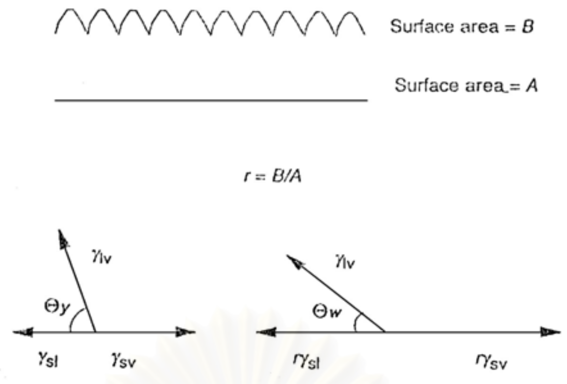


Figure 2.19 The Wenzel relationship [18].

Contact angle measurements are dependent upon the direction in which the measurement is made. When a drop is laid down upon a surface and advances over the surface as it spreads, the contact angle in this situation is known as the advancing contact angle or recently advanced angle. If liquid is withdrawn from a drop that has already come into equilibrium with the surface, the contact angle is known as the receding contact angle or recently retreated angle. In general, the advancing angle is larger than the receding angle. The phenomenon of having a different contact angle under advancing and receding conditions is known as contact angle hysteresis, as expressed in Equation 2.17.

$$H \equiv \theta_a - \theta_r \qquad (2.17)$$

where H is hysteresis, θ_a is advancing contact angle and θ_r is receding contact angle.

A number of reasons for contact angle measurements are hysteretic, specifically: nonhomogeneous surface chemistry, surface roughness, and molecular rearrangement in the solid induced by liquid and vice versa.

2.6.5 The Fowkes Hypothesis [19]

Fowkes proposed a separation of the surface energy of a material into the potential energy of interaction. The Fowkes hypothesis is a first order approximation which, simply stated, is that the surface energy of a material can be divided into component parts. Thus :

$$\gamma = \gamma^{d} + \gamma^{p} + \gamma^{i} + \ldots\ldots \qquad (2.18)$$

where γ^{p} is the polar contribution to the surface energy, γ^{i} is the dipole induced dipole contribution to the surface energy and γ^{d} is the dispersion force contribution to the surface energy. Fowkes also made a fundamental hypothesis important to the study of interface and adhesion, namely that materials exhibiting only dispersion force interactions interact with other surface by only those interactions. It was also Fowkes' contention that polar force and dipole-induce dipole force were insignificant when one of the two materials at an interface was non-polar. Mathematically this can be stated:

$$\gamma_{12} = \gamma_{1} + \gamma_{2} - 2(\gamma_{1}^{d} + \gamma_{2}^{d})^{1/2} \qquad (2.19)$$

where γ_{1} and γ_{2} are surface energies as we have previously defined them and γ_{1}^{d} and γ_{2}^{d} are the dispersion force components of the surface energy of material *1*, and *2* respectively. Applying Equation 2.19 to a solid-liquid interface gives :

$$\gamma_{sl} = \gamma_{s} + \gamma_{l} - 2(\gamma_{s}^{d} + \gamma_{l}^{d})^{1/2} \qquad (2.20)$$

If π_e is assumed that to be small and $\gamma_{lv} \approx \gamma_l$, γ_s can be eliminated by combining Equation 2.20 and Young ‘s equation, we can write.

$$\gamma_{lv}(1+\cos\theta) = 2(\gamma_s^d + \gamma_l^d)^{1/2} \qquad (2.21)$$

Equation 2.21 sometimes called the Young – Good – Girifalco – Fowkes equation. Fowkes’s suggestion brought interfacial tension closure to the microscopic world. From the point of view of contact angle measurement, it gave rise to a number of different equations, besides the dispersion component, the other component of the interfacial tension. Hydrogen bonding and interaction between permanent dipoles were, in general, lumped together in a so-call polar component. Several different treatments extended the geometrical mean approach of Equation 2.21 also to the polar term, as follows :

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d + \gamma_l^d)^{1/2} - 2(\gamma_s^p + \gamma_l^p)^{1/2} \qquad (2.22)$$

where the subscript p indicates the polar component [19].

2.6.6 Polarity [20]

The separation of the total surface tension or energy into two types of forces across an interface can be described as follows. Since an interface is a phase boundary, attractive force exists between the two phases. They may be classified as two general types: dispersion and specific. The dispersion forces are ubiquitous in nature, arising from electron orbitals, which are present in all materials. The specific or non-dispersion forces are present only in some substances. They can arise from a variety of causes, the primary ones being di-pole or polar attractions, although, there can be other causes. It is conventional to lump these specific forces together and call them “polar” forces.

With the dependent measurements, the surface energy can be resolved into these two components, thus yielding important information regarding the nature of the surface forces of both liquids and solids. To characterize the polarity of a solid, two liquids of known polarity and surface tension are required. Water and methylene iodide are commonly used for this purpose, but other fluids can be used. To determine the polarity of a liquid two known solids are required. Pure polyethylene pellets and pure teflon pellets are usually used to characterize the materials. Knowing contact angles for two known materials enables solving the equation for determining not only surface polar component.

The surface tension or energy of a liquid and a solid is regarded as being composed of two contributions, dispersion and polar, such that

$$\gamma_l = \gamma_l^d + \gamma_l^p \tag{2.23}$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{2.24}$$

where γ_l is the surface tension of fluid

γ_s is the surface energy of solids

γ_l^d , γ_l^p are dispersion and polar surface tension of liquid, respectively

γ_s^d , γ_s^p are dispersion and polar surface energy of solid, respectively

To determine the polarity of solid and liquid one solves the Equation 2.25 and determine the percentage polarity as Equation 2.26:

$$\gamma(1+\cos\theta)/2 = (\gamma_s^d \gamma_l^d)^{1/2} + (\gamma_s^p \gamma_l^p)^{1/2} \qquad (2.25)$$

and then :

$$\%Polarity = \frac{100 \times Polar\ component}{Total\ surface\ energy} \qquad (2.26)$$

2.6.7 Wetting Tension [20]

The wetting tension of a given solid is an estimate of its surface energy. Even though the wetting tension value is usually smaller than the surface energy, it is often equated with it and is a satisfactory measure for the purpose of evaluating corona treated film.

The wetting tension concept can be explained by a simple test. In the test, droplets of liquids, whose surface tension values decrease from one liquid to the next ($\gamma_{l_1} > \gamma_{l_2} > \ldots > \gamma_{l_n}$) are placed on the sample surface, and their contact angles are measured. The contact angles decrease from liquid to liquid until one liquid has a zero contact angle. Therefore, the wetting tension of solid is considered equal to the surface tension of the liquid that just exhibits a zero contact angle. The liquid surface tension was given a special name, the critical wetting tension of the solid surface or γ_c. This method is known as the Zisman plot. The mathematical formulation of the Zisman relation is as follows:

$$\cos\theta = 1 + b(\gamma_c - \gamma_{lv}) \qquad (2.27)$$

where θ is the contact angle, γ_{lv} is the interfacial tension between the probe liquid and air saturated with the vapor of liquid, γ_c is a critical wetting tension and b is the slope of the line.

2.6.8 Adhesion [21]

As a definition, adhesion is the joining together of two dissimilar materials, while cohesion is the joining together of different portions of the same materials.

When printing, beside the wettability of the surface required for the image, sufficient adhesion of the printing ink film to the substrate is necessary.

The forces between the molecules of the solid and of the liquid must be stronger than the attraction forces among liquid molecules themselves. Thermodynamically expressed this means:

$$Adhesion\,Work,\ W_A > Cohesion\,Work,\ W_C\ (\overset{\wedge}{=} 2\gamma_s) \qquad (2.28)$$

The adhesive forces are based on the fact that forces originating from any surface of a condensed phase will bind other substances to this surface. Binding may also occur because the forces of the surface are only partly satisfied.

Dupre’ described reversible adhesion work W_A between liquid and solid per unit of surface as follows:

$$W_A = \gamma_s + \gamma_l - \gamma_{sl} \tag{2.29}$$

when the Young-Dupre’ equation $(\gamma_s = \gamma_{sl} + \gamma_l \cos\theta)$ is applied, Equation 2.26 for the adhesion work of a liquid at a solid (at normal temperatures, which do not cause strong vapour condensation) results, when $\theta > 0$ and $\gamma_l >> \gamma_c$

$$W_A = \gamma_l (1 + \cos\theta) \tag{2.29}$$

2.7 Literature Review

Naitoh et al. [22] studied an aqueous-base developable photoresist based on photoinduced cationic polymerization prepared by copolymerization of glycidyl methacrylate (GMA) and methacrylic acid (MAA). The resist comprising the copolymer, vinyl ether monomer as a bifunctional crosslinker and diphenyliodonium 9,10-dimethyoxy-anthracene-2-sulfonate as a photoacid generator exhibited the sensitivity of 20 mJ cm^{-2}. A good pattern profile with high resolution was attained by exposure to a 365-nm light followed by a postexposure bake at 60°C for 3 min.

Moon et al. [23] studied the copolymers of *p*-hydroxystyrene and *p*-(2-vinyloxy ethoxy) styrene (PVESs) containing a photoacid generator had either positive or negative working behavior, depending on process conditions such as prebaking temperature or exposure energy. The pendant vinyl ether group reacted with the hydroxyl group of phenol with the aid of thermal energy to form cross-linked networks. The cross-links are decomposed by acid. The vinyl ether groups also underwent the competing reactions of cationic polymerization and acidolysis by photogenerated acids. The complicated behavior of PVES was determined by a combination of these reactions.

Taguchi et al. [24] studied a new positive resist composing a bifunctional vinyl ether monomer as a crosslinker and a photoacid generator and an acidic base resin was investigated. This resist system utilized the unique reaction of the vinyl ether monomer that formed crosslinks of the base resins by prebaking and the crosslinks were decoupled by acidolytic reaction via generation of an acid upon exposure. It is found that this resist system has high thermal resistance up to 180°C against both pattern deformation and resist thickness loss.

Taylor et al. [25] studied the synthesis, properties and lithographic behavior of a new class of chemically amplified, positive tone, aromatic methacrylate resist incorporating the tetrahydropyranyl protecting group bound to base-solubilizing carboxylic acid moieties. The resulting copolymers of benzyl methacrylate (BMA) and methacrylic acid (MAA) were extremely soluble in aqueous base solution when the MAA concentration exceeded 35 mol%, thus affording positive tone patterns. This class of resins led low absorbance at 248 nm needed for patterning ≥ 1-μm-thick films. The resolution was significantly influenced by the sensitizer, postexposure heating, and development condition.

Watanabe et al. [26] studied the three-component photoresists comprising alkaline developable base polymer, an aliphatic divinyloxy alkane cross-linkers with cyclic group and photoacid generators were developed. Poly(methacrylic acid-*co*-tricyclo[5.3.2.0]decanyl methacrylate)^{2,6} or (poly(MAA-*co*-TDMA)) was used as a base polymer. 1,4-divinyloxy methylcyclohexane (DVMCX) and 2,2×-bis(4-(2-vinyloxyethoxy) cyclohexyl) propane (BVECP) were used as a cross-linker. Bis-(*p*-(*tert*-butylphenyl))iodonium trifluorate (BBI-Otf) was used as a photoacid generator (PAG). These photoresists have high transparency after prebaking. The high photoresist sensitivity of 5 mJ cm^{-2} and 18 mJ cm^{-2} for ArF excimer laser lithography were achieved in DVMX and BVECP photoresist, respectively.

Hotta and Yamaoka [27] studied negative-working photopolymers based on a cationic polycondensation mechanism. These photopolymers were composed of a poly(*p*-hydroxystyrene) matrix, a hexamethoxy methylmelamine crosslinker and a

2,4,6,-tris(trichloromethyl)-1,3,5,-triazine-coumarin dye combination as a photoinitiator. The photopolymers are highly sensitive to 488-nm Argon-ion laser light, because they used a chemically amplified reaction that were not sensitive to ambient oxygen.

Ueda et al. [28] studied a positive working photoresist based on octa-O-*tert-butyl carbonated C-hexylcalix[4]*resorcinarene (*t*-BOC-*h*-C4) and *p*-nitrobenzyl-9,10-dimethyoxy-anthracene-2-sulfonate (NDS) as a photoacid generator. These photoresist was exposed to 365-nm light and postbaked at 90°C for 2 min, followed by developing with a 1% aqueous tetramethylammonium hydroxide (TMAH) solution at room temperature.

Stahlhofen et al. [29] studied a light-sensitive mixture which contained a water-insoluble, aqueous-alkali soluble binder, a light-sensitive o- or p-quinone-diazide or a mixture of a compound which generates or splits off an acid on exposure to light and a compound having at least one C-O-C group, which can be cleaved by acid, and a phenol compound having 1 to 3 benzene nuclei, which are mutually linked by single bonds, carbonyl groups, ether groups, thioether groups or optionally substituted methylene groups, and having at least one phenolic hydroxyl group and at least two substituents of the formula $–CH_2OR$, in which R is hydrogen or a lower alkyl or acyl group. The mixture was used for the preparation of light-sensitive copying material, preferably for the preparation of planographic printing forms. The addition of the phenolic compound had the effect that the developed printing forms could be baked at lower temperatures than hitherto in order to extend the printing run.

Stahlhofen et al. [30] studied a light-sensitive mixture, which was composed of a light-sensitive compound, for example, an o-quinone-diazide or a diazonium salt polycondensate, or a light-sensitive combination of compounds, for example, a photolytic acid donor and an acetal compound or orthocarboxylic acid compound which could be cleaved by acid, and of a novolak having halogenated phenol units was described. The mixture was preferably used for the preparation of printing plates, in particular planographic printing plates, which had an improved resistance to aqueous alkaline developer solutions, gasoline hydrocarbons and fountain solutions containing alcohol.

Chandross et al. [31] studied photosensitive bodies that were sensitive to ultraviolet radiation and that exhibited excellent contrast were formed from base soluble polymers such as poly(methyl methacrylate-co-methacrylic acid) physically mixed with base insoluble materials such as o,o′-dinitrobenzyl esters. The base insoluble esters decomposed upon irradiation to form base soluble entities in the irradiated regions. These irradiated portions were then soluble in basic solutions that were used to develop the desired image.

Kempf et al. [32] studied a process for producing negative or positive images from a photohardenable electrostatic master comprising an electrically conductive substrate bearing a photohardenable layer containing a photoinhibitor and a visible light sensitizer wherein the negative image was prepared by imagewise exposing to visible radiation, charging electrostatically the master plate, developing the charged image with an electrostatic toner, e.g., liquid electrostatic developer, and transferring the toner image to a surface, e.g., paper. The positive image was prepared by imagewise exposing to ultraviolet radiation, then exposing overall to visible radiation followed by the same aforementioned method. Multiple images could be prepared from the same master as well as color proofs using different color toners or developers and transferring in register over the original image.

Blanchet-Fincher et al. [33] studied high resolution, photosensitive electrostatic master which is positive-working with a single imagewise exposure comprising conductive support bearing a layer of photosensitive composition consisting essentially of (a) at least two polymeric binder, at least one binder having a Tg greater than 80 °C, and at least one binder having a Tg of 70 °C or less. (b) a hexaarylbiimidazole photooxidant, (c) leuco dye, preferably stabilized, oxidized by (b), (d) a nonionic halogenated compound, preferably a hydrocarbon, and (e) at least one compatible plasticizer. A process of making positive images by a single imagewise exposure is described. The master is useful in making proofs that duplicate the image achieved by printing, and manufacture of printed circuit boards, etc.

Uenishi et al. [34] studied a positive type photoresist composition which comprised an alkali soluble novolak resin and at least one light-sensitive material represented to provide a resist pattern with high resolution, high reproduction fidelity, desirable sectional shape, wide latitude of development, high heat resistance and high storage stability.

Bantu et al. [35] studied the simple, environmentally friendly photoresist developers and strippers which were disclosed for free radical-initiated, addition polymerizable resists, cationically cured resists and solder masks and Vacrel photoresists. In all cases both the developers and the strippers included gamma butyrolactone, propylene carbonate and benzyl alcohol, optionally also including a minor amount of methanol, ethanol, isopropyl alcohol, propylene glycol monomethylacetate, ethylene glycol monomethyl ether, formamide, nitromethane, propylene oxide, or methyl ethyl ketone, acetone and water.

Lazarus et al. [36] studied a positive working deep UV sensitive photoresist which provided improved critical dimension stability during prolonged periods of post exposure delay before baking. It comprised an acid stable polymer which was insoluble in water but normally soluble in an aqueous alkaline medium, a photo acid generator exemplified by the tri-(2,1,4-diazonaphthoquinonesulfonate) ester of 3,5-dinitro-2,6-dimethylol para cresol, and a mixed carbonate ester of tertiary butyl alcohol and a poly(hydric phenol), which is an acid labile compound which inhibited the dissolution of the normally soluble polymer in the said alkaline solution.

Zampini et al. [37] studied a new photoactive compound for use in the formulation of a photoresist comprises a bisphenol compound having an alkyl linkage substituted with a heterocyclic group. The new photoactive compound may be admixed with an alkali soluble resin to formulate a photoresist composition. The new photoactive compounds exhibited enhanced long term solubility in conventional photoresist solvents.

Burberry et al. [38] studied a lithographic printing plate, which was comprised of an anodized aluminum support having thereon an oleophilic image forming layer comprising an infrared-absorbing agent dispersed in a film-forming cyanoacrylate polymer binder. The plate was imagewise exposed to a focused high-intensity infrared laser beam, which removed the oleophilic image-forming layer by thermal ablation to thereby reveal the underlying hydrophilic support surface. The cyanoacrylate polymers provided superior performance due to their combination of low decomposition temperature, good ink receptivity, good adhesion to the support and good wear characteristics.

Barclay et al. [39] studied novel copolymers and photoresist compositions that contained such copolymers as a resin binder component. Preferred copolymers included three distinct repeating units: 1) units that contained acid-labile groups; 2) units that were free of both reactive and hydroxy moieties; and 3) units that contributed to aqueous developability of a photoresist containing the copolymer as a resin binder. Photoresists of the invention exhibited surprising lithographic improvements including substantially enhanced plasma etch resistance and isolated line performance as well as good dissolution rate control.

Miyazaki et al. [40] studied an additive process for producing printed wiring boards, using a developer comprising a chlorine-free organic solvent and an alkaline aqueous solution and as a resist material of a copolymer of methacrylic acid and methyl methacrylate or the like. The production steps were simplified even if a substrate having a large area was used, and abolishment of chlorine-containing organic solvent as a developer became possible.

Salvin et al. [41] studied photopolymerisable compositions which comprised a) 20 to 80% by weight of a specific film-forming, acid group-containing acrylate of higher molecular weight, which was neutralised with ammonia or an amine or an organic base, at least 10% by weight of component a) consisting of a acrylate of higher molecular weight, which was derived from a reaction product of a polymolecular epoxy resin that is advanced with a bisphenol and an ethylenically unsaturated monocarboxylic acid and after subsequent reaction with a cyclic anhydride of an organic polycarboxylic acid, b) 0.1 to 15% by weight of a photoinitiator, c) 1 to 25% by weight of optional components, and d) water, as well as e) at least one additional optional (meth)acrylate monomer or (meth)acrylate oligomer or a vinyl compound that could be crosslinked with light. The compositions contained no additional polymolecular polymer binders and which could be used as aqueous applicable photoresist compositions, preferably for coating printed circuit boards. The coating so obtained therefrom were non-tacky after drying and had good edge coverage.

Shimizu et al. [42] studied a transparent plastic sheet obtained by copolymerizing 100 parts by weight of methyl methacrylate with 0.1 to 2.0 parts by weight of methacrylic acid and 0.1 to 1.5 parts by weight of glycidyl methacrylate, and having a thickness of not greater than 4 inches, wherein the angular deviation satisfied specified conditions according to the thickness of the sheet and wherein the degree of swelling was not greater than 2.50. This transparent plastic sheet shows neither coloring nor sink marks on the surface, had excellent craze resistance and low long-term water absorption percentage, and was hence suitable for use as an aircraft windshield.

Hagen et al. [43] studied a negatively operating photoresist composition comprising a polyimide precursor and a photoinitiator for polymerizing olefinic double bonds. The composition could be developed by means of aqueous-alkaline developers for photoresists, which were free of organic solvents.

Gybin et al. [44] disclosed a universal method to make photosensitive polymers from poly(vinyl alcohol) and poly(vinyl pyridine), which generally did not require final purification. These polymers comprised a heterocyclic, light-sensitive pendant group including a moiety.

Takahashi et al. [45] studied a photosensitive resin composition comprising a) a binder polymer and/or a prepolymer; b) an ethylenically unsaturated compound; c) a radical producer capable of producing a free radical upon exposure to ultraviolet rays of 300 to 400 nm; d) an anthraquinone dye capable of exhibiting a color change upon exposure to ultraviolet rays in the presence of the radical producer, c). This photosensitive resin composition, upon exposure through a negative mask to UV-rays of a wavelength in a specific range and of a quantity larger than a threshold value, could form a photoresin product having image and non-image portions, which were different in color from each other; hence, this composition could advantageously be used in the fields of printing plates and resists.

Vermeersch et al. [46] invented a method for making a lithographic printing plate comprising the steps of: 1) image-wise exposing to light, and an imaging element comprising (a) a hydrophilic surface of a lithographic base and an image forming layer comprising hydrophobic thermoplastic polymer particles capable of coalescing under the influence of heat and dispersed in a hydrophilic binder, and (b) a compound capable of converting light to heat, the said compound comprising in the said image forming layer or a layer adjacent thereto; and 2) developing a thus obtained image-wise exposed imaging element by mounting it on a print cylinder of a printing press and supplying an aqueous dampening liquid and/or ink to the said image forming layer while rotating the said print cylinder.

Rahman et al. [47] studied a method for producing a film forming, fractionated novolak resin having the consistent molecular weight and superior performance in a photoresist composition, by isolating such a novolak resin fraction. A method is also provided for producing the photoresist composition from such a fractionated novolak resin and for producing semiconductor devices using such a photoresist composition.

Taylor et al. [48] developed novel polymers and chemically-amplified positive-acting photoresist compositions that contain such polymers as a resin binder component. Preferred polymers of the invention included one or more structural groups that were capable of reducing the temperature required for effective deprotection of acid-labile moieties of the polymer.

Merritt et al. [49] studied positive resists sensitive to UV, EB and X-ray radiation which were alkaline developable formulated from a polymer material comprising recurrent structures having alkaline soluble groups pendant to the polymer backbone, a portion of which groups were substituted with acid labile groups.

Ehrhart et al. [50] studied photopolymerizable plastisol, an organosol photoresist, and solder mask coating compositions. These compositions included an ethylenically unsaturated photopolymerizable liquid plasticizer; a particulate, thermoplastic resin is dispersed in the plasticizer, the said resin having midpoint Tg greater than 110°C and an acid number greater than 110; a tertiary amine stabilizer; and a photoinitiator. The organosol included a diluent along with the other ingredients.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1 Monomers

Methyl methacrylate (MMA) was supplied by Ethernal Resin Co., Ltd. Bangkok, (Thailand). It was purified by removing the added inhibitor before use. It was washed twice with 10% aqueous sodium hydroxide in a seperating funnel. The aqueous phase was drained off, and the monomer phase was washed with distilled-deionized water until pH 7 was obtained. Then anhydrous sodium sulfate (100 g l^{-1}) was added to adsorb the remained amount of water in the monomer phase. Finally, the dried monomer was passed through an activated aluminum oxide column, neutral and basic type from Fluka, Steinheim, Switzerland. The purified methyl methacrylate (MMA) was stored in a brown capped bottle under nitrogen atmosphere and kept in a refrigerator at 5°C.

Methacrylic acid (MAA) was supplied by Thai Mitsui Specialty Chemicals Co., Ltd. Bangkok, (Thailand).

Poly(vinyl alcohol) (PVA-205) was supplied by Siam Resin & Chemical Co., Ltd. Bangkok, (Thailand).

3.1.2 Initiator

Benzoyl peroxide (BPO) (with 25% H_2O) from Merck Co., Ltd. Honenbrunn, Germany. It was collected in a bottle sealed with aluminium foil to protect from the radiation from sun light and then stored in a refrigerator at 5^oC.

3.1.3 Photoinitiators

2-Hydroxy-2-methyl-1-phenyl-propan-1-one(Ciba® Darocur® 1173) was from Ciba Specialty Chemicals, Bangkok, (Thailand) has the following property: molecular weight 164.2, melting point 4°C, boiling point 80-81°C, flash point>100°C density 1.08 g cm^{-3}, viscosity (at 20°C) 25 mPa s, UV absorbance at 244 nm

Benzophenone (Ciba® Darocur® BP) was from Ciba Specialty Chemicals, Bangkok, (Thailand), having molecular weight 182.2 and melting point 47□49 °C.

3.1.4 Reactive diluents

Tripropylene glycol diacrylate (TPGDA) [2-Propenoic acid,(1-methyl-1,2-ethanediyl)bis[oxy(methyl-2,1-ethanediyl)] ester] was from UCB chemicals, Bangkok (Thailand), having a Hoppler viscosity at 25°C 15 mPa s, density 1.05 g cm^{-3}, and a formula weight 300.

Trimethylol propane ethoxylate triacrylate (TMPEOTA or Ebacryl® 168) [Poly[osy-1,2 ethanediyl, alpha,-hydro-omega,-[(1-oso-2-propenyl)oxy]]-ether with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol(3:1)] was from UCB chemicals, Bangkok (Thailand), having a Hoppler viscosity at 25°C 80 mPa s, density 1.09 g cm^{-3}, molecular weight (theoretical 450), and a formular weight of 428.

3.1.5 Pigments

Phthalocyanine (Ciba® **ORACET®** Blue G) was from Ciba Specialty Chemicals, Bangkok, (Thailand), melting point 187°C.

Anthraquinone (Ciba® **ORACET®** Red BG) was from Ciba Specialty Chemicals, Bangkok, (Thailand), melting point 189°C.

3.1.6 Solvents

1. Isopropyl alcohol (IPA), Commercial grade: Merck, colorless liquid, b.p. 82.4°C, and a formular weight 60.1
2. Diethyl ether, Analytical grade: Labscan Asia Co., Ltd., colorless liquid, purity 99.5 % , formular weight 74.12, and b.p. 34.4°C
3. Acetone (C_3H_6O), Analytical grade: Merck, colorless liquid, M = 58.08 g mol^{-1}.
4. Methyl ethyl ketone ($C_4H_8O_6$), Commercial grade: Grand Chemical Inc., colorless liquid, b.p. 79.0 °C, M = 72.11 g/mol, D = 0.804 g cm^{-3}

5. Tetrahyldrofuran (THF), HPLC grade: Labscan Asia Co., Ltd., colorless liquid, assay(GC) 99.8 %, formular weight 72.11, and b.p. 66.0 °C

6. d_6-dimethylsuphoxide(d_6-DMSO), NMR grade: Fluka, Steinheim, Switzerland.

3.1.7 Other Chemicals

1. Aluminium oxide (Al_2O_3), Chromatographic grade: Fluka, Steinheim, Switzerland.

2. Sodium hydroxide anhydrous pellets (NaOH), Analytical grade: Carlo Erba, Milano, Italy.

3. Sodium sulphate anhydrous (Na_2SO_4), Analytical grade: Carlo Erba, Milano, Italy.

4. Oleic acid ($C_{18}H_{34}O_2$), Analytical grade: Fluka, Steinheim, Switzerland.

5. Acetic acid, Analytical grade: Fluka, Steinheim, Switzerland.

6. FUJI FILM Developer DN-3C for negative working plates (an alkaline solution), FUJI photo film Co., Ltd., Tokyo, Japan.

7. Gum Arabic FUJI GU-7, FUJI photo film Co., Ltd., Tokyo, Japan.

8. Acid Fountain Solution ANCHOR, California, USA.

9. Panorama Sheetfed Ink, PR-1 Magenta, A.S. INK & CHEMICAL BANK Co., Ltd., Korea.

10. 610 Scotch Cellophane Tape, by 3M, USA.

3.2 Glassware

1. Four-necked round bottle flask 500 cm^3.
2. Reflux condensor.
3. Thermometer
4. Thermoadapter
5. Nitrogen gas tube
6. Other general laboratory glassware

3.3 Equipment

1. Digital thermostat oil bath : Yamato BF600, Japan
2. Mechanical stirrer : Ika Werker RW20, Germany
3. Cooling circulator : Hakke SK55, Berlin, Germany
4. Digital tachometer : Digicon DT-240P, U.S.A.
5. Vacuum oven : Hotpack 273 700, P.A., U.S.A.
6. Hotplate magnetic stirrer : Snijders Scientific 334532, ilberg, Holland
7. Heating mentle : Horst, Germany
8. Stirrer : Semicircular Teflon Paddle
9. FT-IR Spectroscopy : Perkin Elmer 1760X, U.S.A.
10. NMR : Bruker DPX-400, Germany.
11. Differential Scanning Colorimeter(DSC) : Netzsch 200, Selb/Bavaria, Germany
12. Gel Permeation Chromatography(GPC) : Water 510, USA.
13. Elemental Analyzer (CHNS/O Analyzer): Perkin Elmer PE2400 Series II, USA.
14. HAAKE Viscometer : Brookfield, Germany

15. Spin Coater : ABLE Co., Ltd., Japan
16. UV exposure : TA SHIANG machine Co., Ltd., Model TS-VPF 32 SP-2, Taiwan
17. Real Time Image Analyzer Stereo Microscope Coupling with Luzex-F Software Programme of Nireo QJ 8500 : Olympus SZH10, Japan
18. Contact angle meter : FACE Kyowa Interface Science Co., Ltd., Model CA-A, Japan
19. Dryer : Casiko 1500, PRC.

3.4 The Synthesis of Poly(methyl methacrylate-*co*-methacrylic acid)

The copolymers of methyl methacrylate(MMA) and methacrylic acid(MAA) prepared by radical copolymerization were carried out in a 500 cm^3 round bottom flask equipped with a paddle stirrer with a rate of 295 rpm, a reflux condensor and a thermometer. The procedure used to prepare the copolymer was as follows. A mixture(130 cm^3) of a specific amount of methyl methacrylate monomer(MMA) and methacrylic acid monomer(MAA) in isopropyl alcohol (IPA) with a monomer concentration of 25 %w/w at 70^{o}C and benzoyl peroxide (BPO) of 1%w/w based on the total comonomer concentration as an initiator. The synthesized copolymers were isolated by precipitating in diethyl ether, dissolution in IPA and then reprecipitating in diethyl ether.

3.4.1 The Effect of the Monomer Ratio

The free radical copolymerization of methyl methacrylate(MMA) and methacrylic acid (MAA) was repeated using the ratios of MMA : MAA as given in Table 3.1

Table 3.1 Various ratios between two monomers for the free radical copolymerization of methyl methacrylate (MMA) and methacrylic acid (MAA).

Runs	**Ratio of MMA : MAA**
T16-90	90 : 10
T16-80	80 : 20
T16-70	70 : 30
T16-60	60 : 40
T16-50	50 : 50

[*] Polymerization is carried out at 1% BPO, 70°C, 16 hours and 295 rpm.

3.4.2 The Effect of the Reaction Time

The copolymerization of methyl methacrylate and methacrylic acid was repeated using reaction times as given in Table 3.2

Table 3.2 Various reaction times for the free radical copolymerization of methyl methacrylate and methacrylic acid.

Runs	Reaction times(hours)
T05	5
T07	7
T13	13
T16	16
T24	24

[*] Polymerization is carried out at MMA:MAA 70:30, 1% BPO, 70°C and 295 rpm.

3.5 Copolymer Characterization

The synthesized copolymers were characterized as below:

3.5.1 Identification of Functional Groups of the Copolymer of Methyl Methacrylate and Methacrylic acid

3.5.1.1 Fourier-Transform Infrared Spectrophotometry

The functional groups of the copolymers were investigated using a Fourier-Transform Infrared Spectrophotometer (FTIR: Perkin-Elmer Infrared Spectrophotometer, model 1760X). The copolymer was ground with the dried KBr powder, and the KBr mixed powder was dried again, pressed and subjected to the FTIR spectrophotometry measurement.

3.5.1.2 Nuclear Magnetic Resonance Spectrophotometry

The ^{13}C-NMR spectra of copolymer solutions (10-15% w/w) in d_6- DMSO (d_6-dimethyl suphoxide) were prepared with 10 mm probe on an Bruker DPX-400 spectrophotometer operating at 400 MHz in the pulsed FT-mode with a wide band modulated proton decoupling. TMS was employed as an internal standard. The probe temperature under the experimental condition was 25°C.

3.5.1.3 Elemental Analysis

The CHO composition in these copolymers were investigated by Elemental Analyzer (CHNS/O Analyzer: Perkin Elmer PE2400 Series II).

3.5.2 Determination of Molecular Weight Average (M_w), Molecular Weight Number Average (M_n) and Molecular Weight Distribution (MWD) by Gel Permeation Chromatography

The sample was weighed accurately 0.005 g in a test tube containing 5 cm^3 of tetrahydrofuran (THF), then sealed with aluminum foil and parafilm. After the sample dissolution was completed, the solution was filtered through a membrane filter with pore size 5 μm before injecting (100 μl) in a 5 cm^3 volumetric flask. Analysis of molecular weight of the copolymer was performed on a WATER 510 with a series of 4 ultra styragel columns having nominal exclusion limits of 10^3, 10^4, 10^5 and 10^6 ⊕ at a controlled temperature of 35°C and equipped with a differential refractometer, using THF as an eluent at the flow rate of 0.7 cm^3 min^{-1} The M_w, M_n and polydispersity (M_w/M_n) were analyzed by the MAXIMA software for GPC by comparing with the standard calibration curves of polystyrene standards having a Mw range of $2.98 \times 10^3 – 2.08 \times 10^7$

The weight average molecular weight (M_w) is related to the weight of the individual molecules as represented by the equation (3.1):

$$M_w = \sum (M_i W_i) / \sum w_i \tag{3.1}$$

where M_i = Molecular weight of polymer in fraction i

W_i = Weight of the polymer in fraction i

and i = Fraction number (from 1 to x)

The number average molecular weight (M_n) is dependent on the number of molecules having each discrete M_n and is represented by the equation(3.2):

$$M_n = \sum W_i / \sum N_i \tag{3.2}$$

where N = the number of molecules in fraction i

The M_w and M_n values may be used to provide an index for the range of molecular weight distribution as follows:

$$M_w / M_n = d \tag{3.3}$$

where d = polydispersity index

3.5.3 Determination of Thermal Properties of the Copolymer of Methyl Methacrylate and Methacrylic Acid by the Differential Scanning Calorimetry

The samples were prepared by drying at 60°C to a constant weight. Glass transition temperature (Tg) of the copolymers was measured using a differential scanning calorimeter (NETZSCH DSC 200), programmed at a heating rate of 20°C min^{-1}. The copolymer was weighed and put in a aluminum pan which is then covered and sealed with another pan, and was put on the sensor with respect to an empty reference pan.

3.6 Surface Coating or Plate Making Procedure

3.6.1 Photosensitive Material Formulation for UV Irradiation

Typical recipes of the photosensitive material were prepared by the formulation as given in Table 3.4

Table 3.4 The formulation to prepare photosensitive materials from the various copolymer binders and dyes

Photosensitive Materials	% By Weight
Binder(copolymer 30% in IPA:MEK 1:1)	58.3
TPGDA	21.0
TMPEOTA	12.2
Darocur 1173	4.3
Darocur BP	3.9
Pigment	0.3
Total	100.0

3.6.2 Measurement of the Viscosity

The viscosity of the photosensitive material solution was measured by Brookfield viscometer (model RVT, with a small sample adapter and spindle number 14) at 25°C under various rates: 1, 2, 4, 8, and 20 sec^{-1} were calculated by multiplying 0.4 with 2.5, 5, 10, 20, and 50 rpm, respectively.

3.6.3 Plate Making Procedure

3.6.3.1 Surface Coating

The photosensitive coating was coated onto an anodized aluminium substrate by spin coating, which formed a smooth film that was overcoated by a 2%PVA solution for preventing the oxidization reaction by varying the binder copolymer. A control stepwedge (UGRA-like wedge) was assembled with an original separation.

3.6.3.2 Exposure

The coated aluminium substrate was exposed with UV radiation at different exposure time for an appropriate exposure.

3.6.3.3 Development

The exposed plate was developed in various developers: acetic acid and aqueous base developer to find the most suitable developer.

3.7 Evaluation of the Quality of the Printing Plate

3.7.1 Image Analyzer

a) %Dot Area and Dot Gain

%Dot area of the original film and the resulting plate, at steps of 40, 50 and 60% dot area were evaluated by an image analyzer, and dot gain curves were reported.

b) Image Characteristics

Dot characteristics were examined using an image analyzer(Lusex-F software Programme of Nireo QJ 8500:Olympus SZH10). Dot characteristics of the original film (a control step wedge, UGRA-like wedge, homemade) and the resulting plate were compared.

3.7.2 Contact Angle Analyzer

To investigate hydrophilic/hydrophobic properties of the resulting plate, the Contact Angle Meter (FACE Kyowa Interface Science Co., Ltd., Model CA-A) was used to measure the contact angles of oleic acid (representing the hydrophobicity of oil) on image area, and water on non-image area on the surface of the resulting plate.

Two contact angle values, the left and right sides of the droplet contact angles were taken. The contact angle values were averaged.

3.7.3 Printing Experiment

The plate was gummed or covered with gum arabic solution during storage. Before printing, the plate was wiped with a moist sponge to remove the gum arabic. The plate was then covered with the fountain solution (20-30 cm^3). An inking rubber roller was rolled on a patch of ink to obtain a full coverage of ink. The ink on the inking roller was then applied to the moist plate. The ink was transferred to the image areas while the non-image area remained uninked. A piece of uncoated paper was then covered the plate and a clean roller was placed on the back of the paper and it was rolled gently over the paper. The images were then transferred to the paper. The print was then evaluated to compare with the original separation film.

3.7.4 Adhesion test

Pressure-sensitive tape (3M 610 brand or equivalent) was pressed onto the coating area of the aluminium substrate surface. The pressure-sensitive tape was pulled straightly and peeled off to observe the coating marks on the tape according to ASTM D 3359-97.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Free-Radical Copolymerization

In this study, the copolymers of methyl methacrylate and methacrylic acid were synthesized by free radical copolymerization. The appropriate condition for such a synthesis of polymer was obtained by varying the ratio of these two monomers and reaction time.

4.1.1 Effect of the Momomer Ratio

The effects of glass transtion temperature, M_w, M_n and polydispersity were investigated by varying the monomer ratio of MMA:MAA as 90:10, 80:20, 70:30, 60:40 and 50:50, respectively, while the other parameters were kept constant as follows:

- isopropyl alcohol concentration : 75% w/w
- monomer concentration : 25% w/w
- initiator (BPO) concentration : 1% w/w
  (based on total comonomer concentration)
- reaction temperature : 70°C
- reaction time : 16 hours
- agitation rate : 295 rpm

4.1.1.1 Effect of the Monomer Ratio on Glass Transition Temperature of the Copolymer

In this study, the glass transition temperature was measured by differential scanning calorimetry. The DSC thermograms of all synthetic copolymers of methyl methacrylate and methacrylic acid with various monomer ratios of 90/10, 80/20, 70/30, 60/40 and 50/50 are shown in Figure 4.1. The Tg range is 116.1°C, 140.4°C, 163.4°C, 156.4°C and 170.8°C, respectively. It can be seen that varying the monomer ratio of the copolymer has a direct impact on glass transition temperature of the resulting copolymers. The Tg of poly(methyl methacrylate) is 115°C and poly(methacrylic acid) is 230°C; Tg of the synthetic copolymer containing these two monomers should be found between the two Tgs of the homopolymers. If the MMA ratio is too high such as MMA:MAA 90:10 (Tg 116.1°C), the Tg value would be shifted close to the Tg of the homopolymer of MMA (115°C). On the other hand, if the MMA ratio is too low such as MMA:MAA 50:50 (Tg 170.8°C), the resulting Tg value would be close to the Tg of the homopolymer of MAA (230°C) more than that of the PMMA (115°C). The other MMA:MAA ratios of 80:20, 70:30 and 60:40, the Tg values are approximately in the middle range for Tg of these two homopolymers.

Table 4.1 and Figure 4.2 present the relationship between Tg and various monomer ratios.

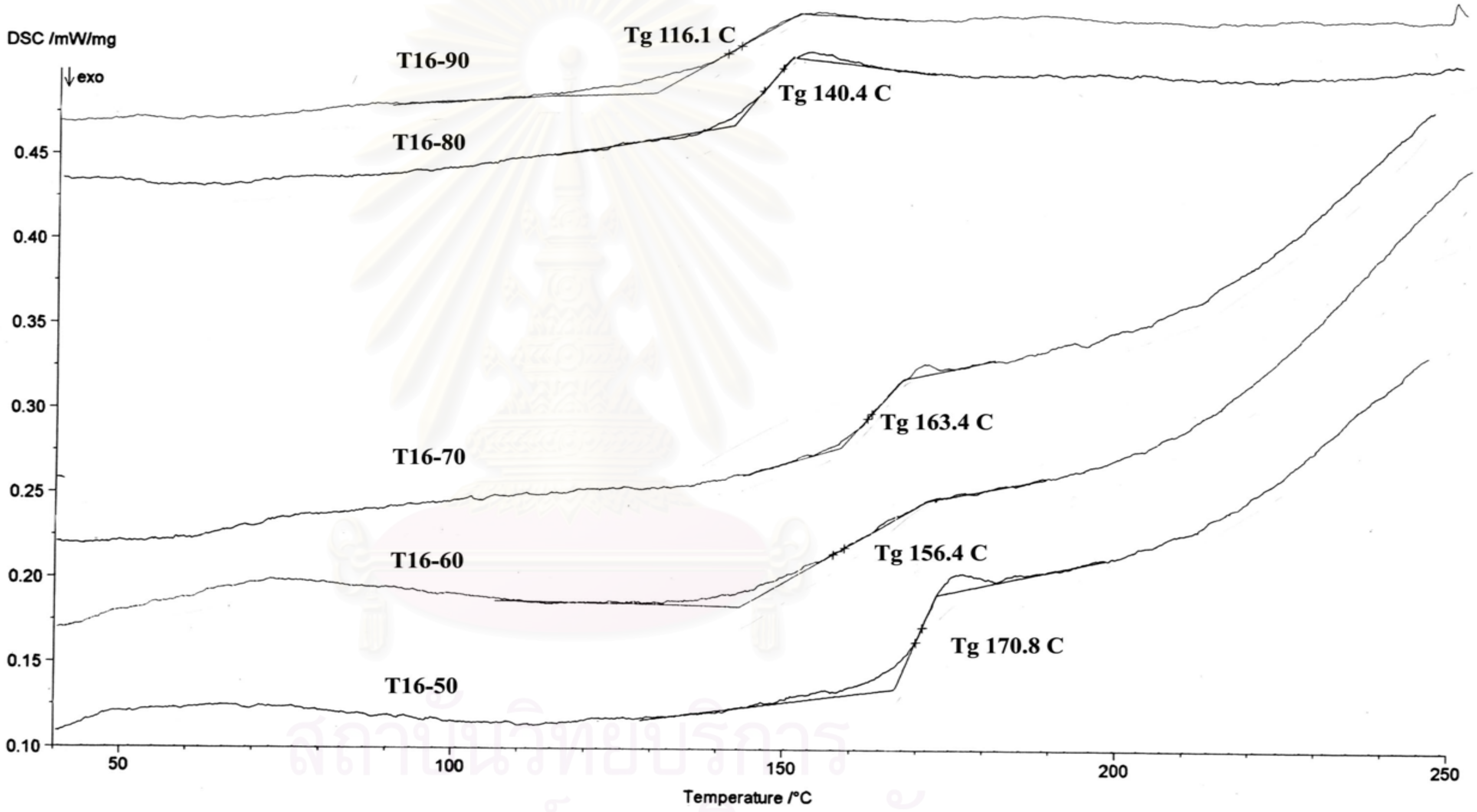


Figure 4.1 DSC traces of the copolymer of methyl methacrylate and methacrylic acid by varying monomer ratios.

Table 4.1 **Effect of the monomer ratio on the glass transition temperature of the copolymers of methyl methacrylate (MMA) and methacrylic acid (MAA).**

Runs	Monomer ratio[a] (MMA:MAA)	Tg (°C)
T16-90	**90:10**	**116.1**
T16-80	**80:20**	**140.4**
T16-70	**70:30**	**163.4**
T16-60	**60:40**	**156.4**
T16-50	**50:50**	**170.8**

[a] Polymerization was carried out at 1% BPO, 70°C, 16 hours and 295 rpm.

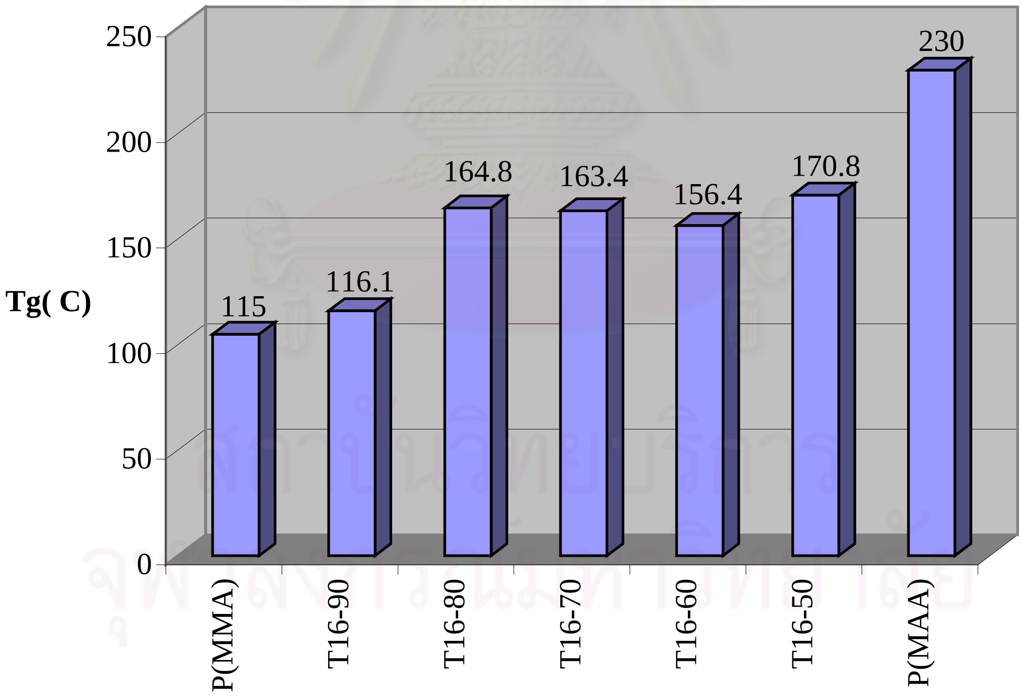


Figure 4.2 **Effect of the monomer ratio on the Tg values.**

4.1.1.2 Effect of the Monomer Ratio on M_w, M_n and Polydispersity of the Copolymer

Analysis of molecular weight of the copolymer was performed on a WATER 510 with ultra styragel columns, using THF as an eluent. The M_w, M_n and polydispersity (M_w/M_n) were analyzed by the MAXIMA software for GPC by comparing with the standard calibration curves of polystyrene standards having a M_w range of $2.98 \times 10^3 – 2.08 \times 10^7$

The weight average molecular weight (M_w) is related to the weight of the individual molecules as represented by the equation (3.1):

$$M_w = \sum (M_iW_i) / \sum w_i \qquad (3.1)$$

where M_i = Molecular weight of polymer in fraction i

W_i = Weight of the polymer in fraction i

and i = Fraction number (from 1 to x)

The number average molecular weight (M_n) is dependent on the number of molecules having each discrete M_n and is represented by the equation(3.2):

$$M_n = \sum W_i / \sum N_i \qquad (3.2)$$

where N = the number of molecules in fraction i

The M_w and M_n values may be used to provide an index for the range of molecular weight distribution as follows:

$$M_w / M_n = d \qquad (3.3)$$

where d = polydispersity index

The weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity (M_w/M_n) of the copolymer of methyl methacrylate at various monomer ratios of MMA/MAA: 70/30, 60/40 and 50/50 are shown in Table 4.2 and Figure 4.3

Table 4.2 The M_w, M_n and polydispersity at various monomer ratios.

Runs[a]	M_w	M_n	Polydispersity (M_w/M_n)
T16-90	128,500	52,000	2.5
T16-80	129,000	58,000	2.2
T16-70	128,000	69,000	1.9
T16-60	123,000	72,000	2.7
T16-50	132,000	62,000	2.1

[a] Polymerization was carried out at 1% BPO, 70°C, 16 hours and 295 rpm.

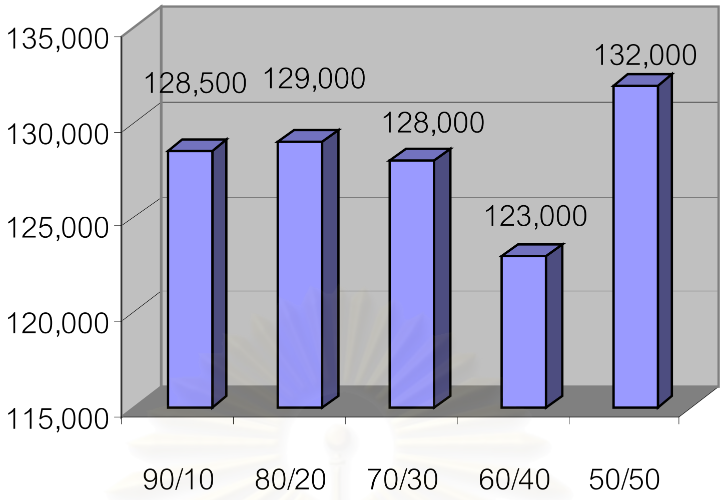


Figure 4.3 Effect of the monomer ratio on average molecular weight.

From Table 4.2 and Figure 4.3, it was found that the monomer ratio affects the M_n of the copolymer tremendously, while M_w is relatively constant. M_w is maximum at the monomer ratio of MMA:MAA 50:50 of 132,000.

4.1.2 Effect of Reaction time

Dependence of glass transtion temperature, M_w, M_n and polydispersity index on reaction time of 5, 7, 13, 16 and 24 hours were investigated. The other parameters were kept constant and the polymerization recipe is as follows:

- isopropyl alcohol concentration : 75% w/w
- monomer concentration : 25% w/w
- initiator (BPO) concentration : 1% w/w
  (based on total comonomer concentration)
- reaction temperature : 70°C

- monomer ratio MMA:MAA : 70:30
- agitation rate : 295 rpm

4.1.2.1 Effect of the Reaction Time on Glass Transition Temperatures of the Copolymer of Methyl methacrylate and Methacrylic Acid

In this study, the glass transition temperatures was measured by differential scanning calorimetry. The summarized DSC thermograms for all synthetic copolymers of methyl methacrylate and methacrylic acid by varying the reaction time of 5, 7, 13, 16, 24 hours are shown in Figures 4.4. The Tg ranges are 158.2°C, 164.8°C, 167.3°C, 146.8°C, and 157.3°C, for T05, T07, T13, T16 and T24, respectively. The results indicate that the variation of the reaction time significantly affects the Tg of the copolymers. The Tg of poly(methyl methacrylate) is 115°C, while poly(methacrylic acid) is 230°C. The Tg of the synthetic copolymer from these two monomers should lie between these of the two Tgs. Table 4.3 and Figure 4.5 present the relation between Tg and various reaction times. The Tg of the copolymer increases when the reaction time is longer. The maximum Tg is found at the reaction time 13 hours, then decreases when the reaction time is longer than 13 hours to a minimum value at the reaction time of 24 hours.

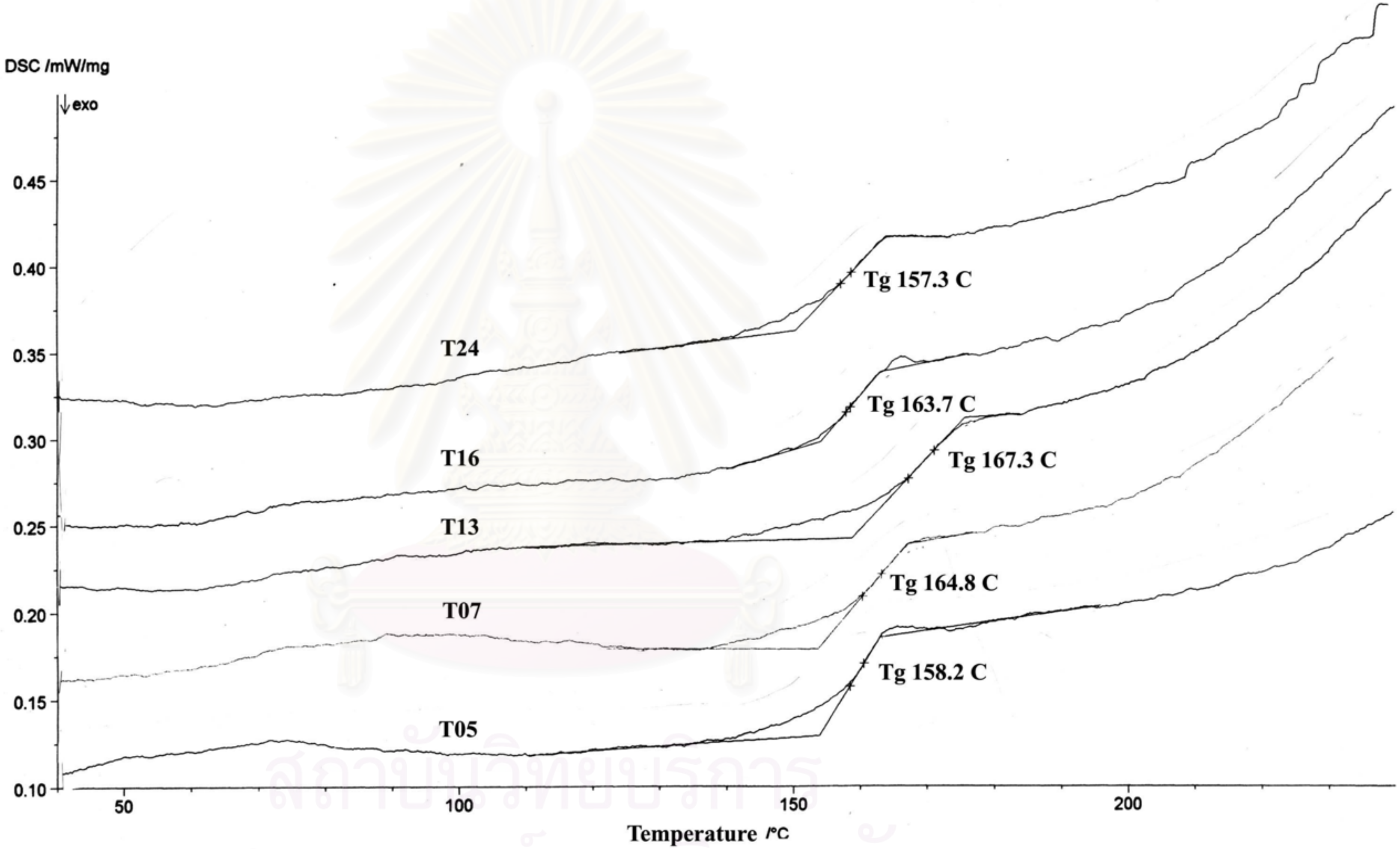


Figure 4.4 The DSC traces of the copolymer of methyl methacrylate and methacrylic acid by varying the reaction time.

Table 4.3 Effect of the reaction time on the glass transition temperature of the copolymer of methyl methacrylate (MMA) and methacrylic acid (MAA).

Runs	Reaction Time[a] (hours)	Tg (°C)
T05	5	158.2
T07	7	164.8
T13	13	167.3
T16	16	163.4
T24	24	157.3

[a] Polymerization was carried out at the ratio of MMA:MAA 70:30, 1% BPO, 70°C and 295 rpm.

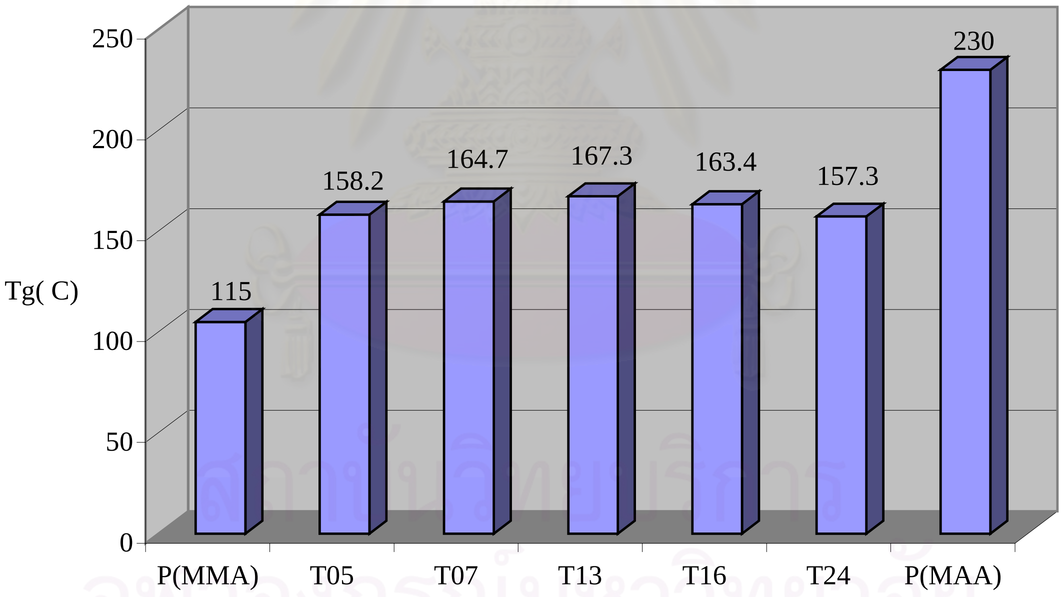


Figure 4.5 Effect of the reaction time on the Tg values.

4.1.2.2 The Effect of the Reaction Time on M_w, M_n and Polydispersity of the Copolymer of Methyl Methacrylate and Methacrylic Acid

Analysis of molecular weight average of the copolymer was performed on a WATER 510 with ultra styragel columns, using THF as an eluent. The M_w, M_n and polydispersity (M_w/M_n) were analyzed by the MAXIMA software for GPC by comparing with the standard calibration curve of polystyrene standards having a M_w range from $2.98 \times 10^3 – 2.08 \times 10^7$

The weight average molecular weight (M_w), number average molecular weight (M_n), and polydispersity (M_w/M_n) of the copolymer of methyl methacrylate at various reaction times: 5, 7, 13, 16 and 24 hours are shown in Table 4.4 and Figure 4.6

Table 4.4 The M_w, M_n and polydispersity of the copolymer of methyl methacrylate and methacrylic acid at various reaction times.

Runs[a]	**M_w**	**M_n**	**Polydispersity (M_w/M_n)**
T05	78,000	36,900	2.1
T07	66,700	35,800	1.9
T13	79,000	35,500	2.2
T16	128,000	37,100	2.9
T24	70,000	36,700	1.9

[a] Polymerization was carried out at the ratio of MMA:MAA 70:30, 1% BPO, 70°C and 295 rpm.

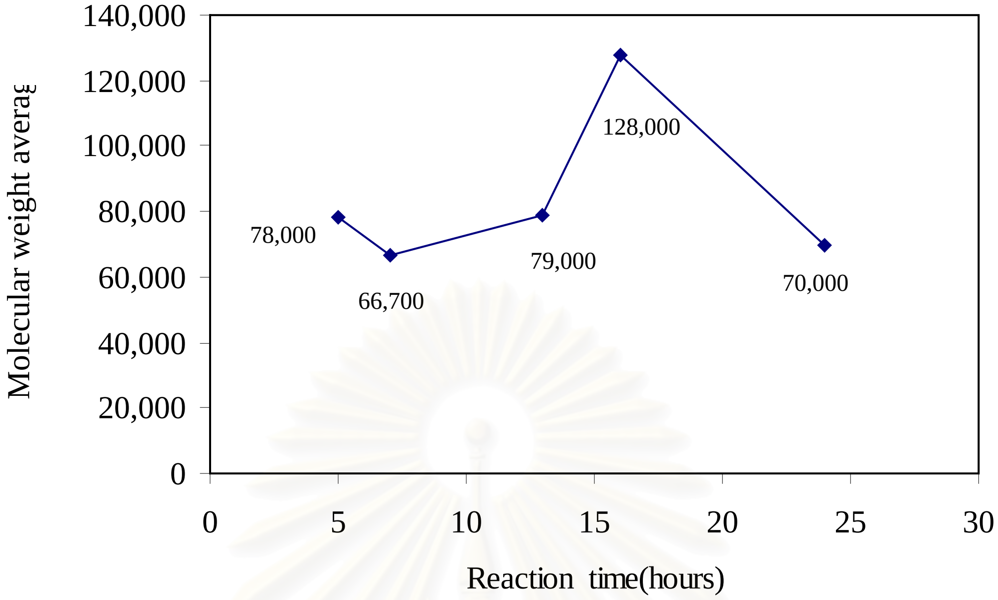


Figure 4.6 The effect of the reaction time on the average molecular weights.

Table 4.4 and Figure 4.6 indicate that the maximum average molecular weight was obtained from the reaction time of 16 hours, and the minimum average molecular weight was found at the reaction time of 7 hours. It was found that the polymerization time affect significantly the average molecular weights of the copolymers.

4.1.2.3 The Effect of the Reaction Time on CHO Composition of the Copolymer of Methyl Methacrylate and Methacrylic Acid

Table 4.5 and Figure 4.7 indicate that the CHO composition of the copolymers of methyl methacrylate and methacrylic acid was prepared from the polymerization time of 13 and 16 hours. It was found that these two copolymers have small difference in the CHO composition, although the M_w of the former(79,000) was only one half of the latter (128,000). The result indicates that the variation of reaction time insignificantly affects the CHO composition of the copolymers.

Table 4.5 Effect of the reaction time on the CHO composition of the copolymer of methyl methacrylate (MMA) and methacrylic acid (MAA).

Runs	Reaction Time[a] (hours)	%C	%H	%O
T13	**13**	**57.986**	**8.007**	**34.007**
T16	**16**	**58.199**	**8.159**	**33.642**

[a]Polymerization was carried out at the ratio of MMA:MAA 70:30, 1% BPO, 70°C and 295 rpm.

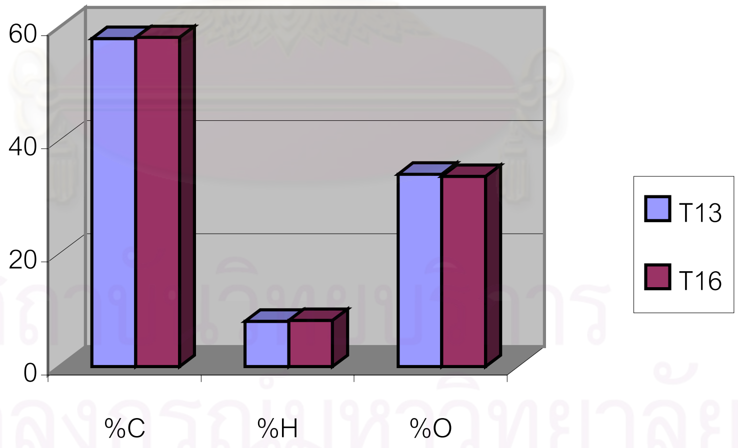


Figure 4.7 %CHO composition of the copolymer of methyl methacrylate and methacrylic acid at various reaction times.

4.1.3 Identification of Functional Groups of the Copolymer of Methyl Methacrylate and Methacrylic Acid

4.1.3.1 Fourier-Transform Infrared Spectrophotometry

To confirm the copolymerization between methyl methacrylate and methacrlic acid, the functional groups were investigated by FT-IR. The IR spectra of the copolymer in KBr pellets were recorded on a Perkin Elmer FT-IR Spectrometer 1760. The existence of the copolymer, which was analyzed by comparing the copolymer spectrum with the reference peaks of the standard poly(methyl methacrylate), as shown in Figures 4.8 and 4.9 shows that IR spectra of both the poly(methyl methacrylate) and the synthesized copolymer are quite similar, the assignments of the important peaks are shown in Table 4.6.

Table 4.6 Important IR peaks of the copolymers of methyl methacrylate and methacrylic acid.

Wave Number, cm^{-1}	Peak Assignment
3591	O–H stretching, broad
3000, 2955	C–H bending CH_3 and CH_2, weak
1733	C=O of ester (MMA), strong
1637	C=O of acid (MAA), weak
1490, 1455, 1389	C–H stretching CH_3 and CH_2, strong
1152	C–O stretching ester, strong

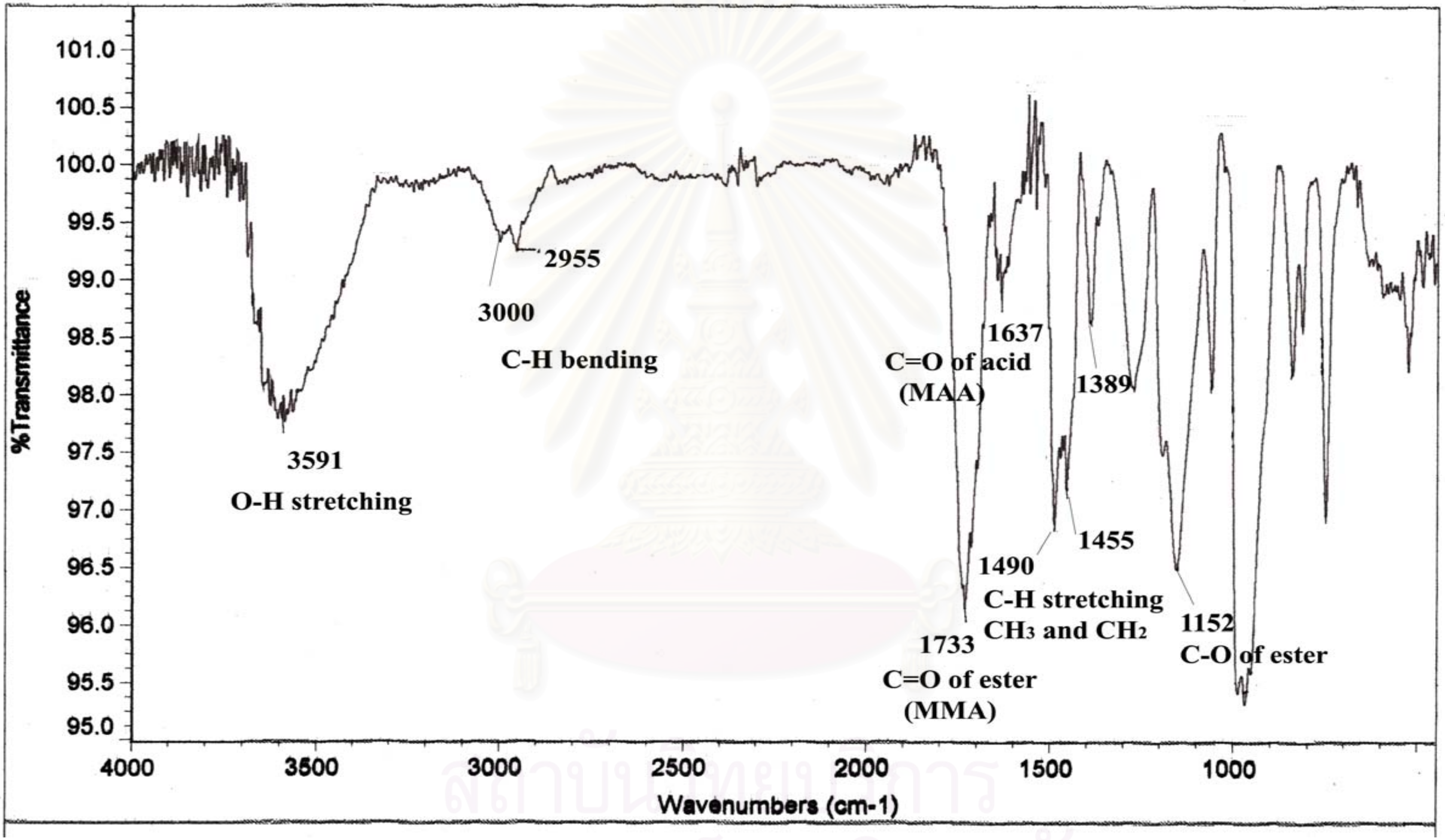


Figure 4.8 Important IR peaks of the copolymer of methyl methacrylate and methacrylic acid.

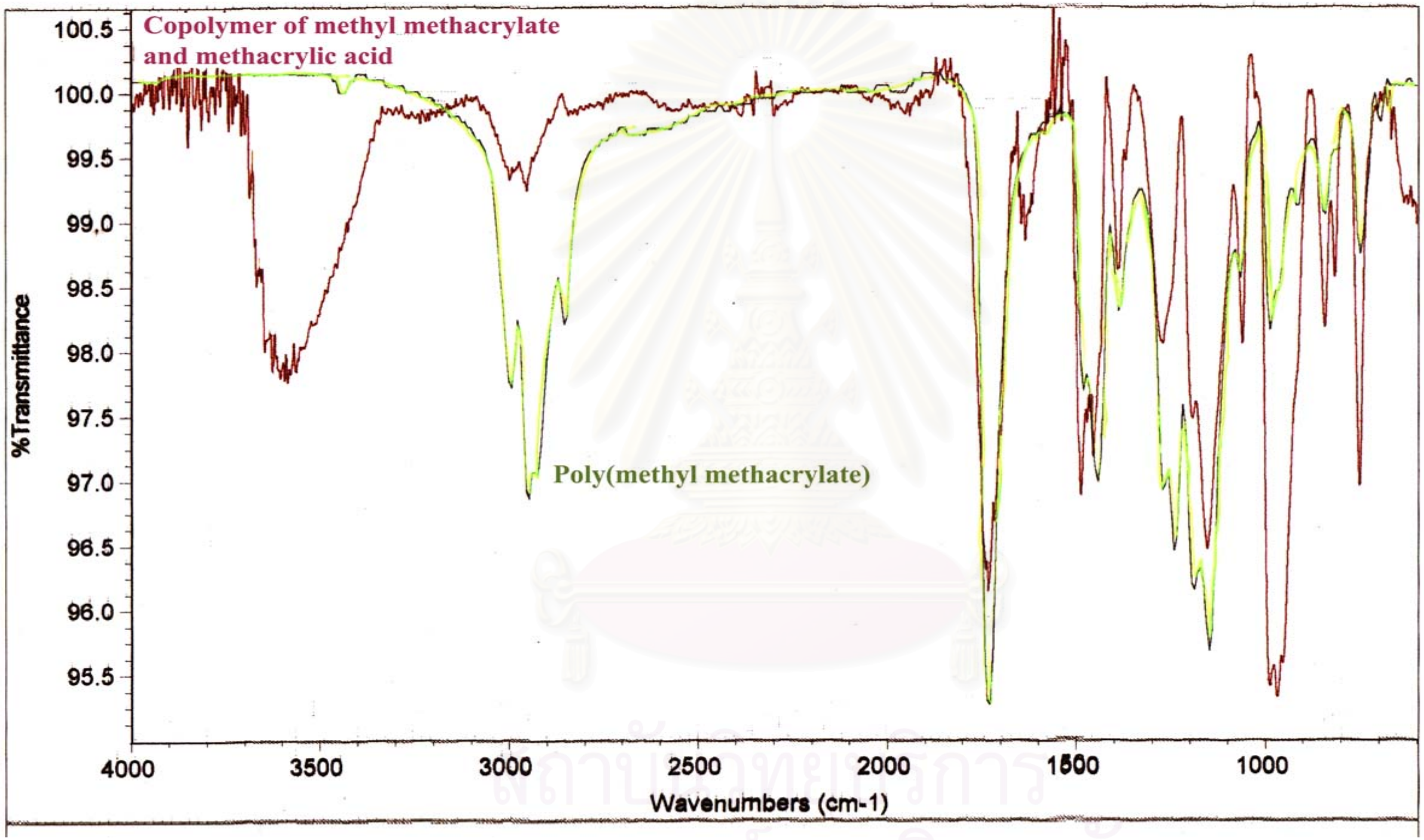


Figure 4.9 Comparison of IR spectra of P(MMA) and the copolymer of methyl methacrylate and methacrylic acid.

4.1.3.2 Nuclear Magnetic Resonance Spectrophotometry

To confirm the carbon positions of the copolymers of methyl methacrylate and methacrylic acid, the ^{13}C-NMR spectrophotometry was used to characterize the copolymer. The ^{13}C-NMR spectra of 10-15% w/w copolymer solutions in d_6-DMSO were recorded on an Bruker DPX-400 NMR spectrometer. The existence of the copolymer was analyzed by comparing the copolymer spectrum with TMS as the internal standard, as shown in Figure 4.10. The ^{13}C-NMR spectrum of the synthesized copolymer, and the assignments of the important peaks are shown in Table 4.7. .

Table 4.7 Important ^{13}C-NMR peaks of the copolymer of methyl methacrylate and methacrylic acid.

Chemical shift, ppm	Peak Assignment of Carbon atom
17.9	$\alpha\text{–}CH_3$
40	d_6- DMSO carbon
45	$-\overset{\vert}{\underset{\vert}{C}}-$
52	$-OCH_3$
55	$-CH_2$
177.6, 178.5	MMA carbonyl (>C=O)
180.2	MAA carbonyl (>C=O)

From the ^{13}C-NMR spectrum, we found that all NMR peaks of the carbon atoms in the copolymer of methyl methacrylate and methacrylic acid (Figure 4.10) show the general peaks that were assigned to the carbon atoms in two types of the monomer units in the copolymer. The d_6- DMSO carbon resonance peak is situated at 40 ppm. The peak of $\alpha-CH_3$ resonance region is situated in 17.9 ppm. The higher resolution of ^{13}C-NMR spectrum of the carbonyl region was from 177 to 181 ppm. The peaks in the range from 177.6 and 178.5 ppm are assigned to MMA carbonyl resonance and the peaks in the range from 180.2 ppm are assigned to the MAA carbonyl resonance[53].

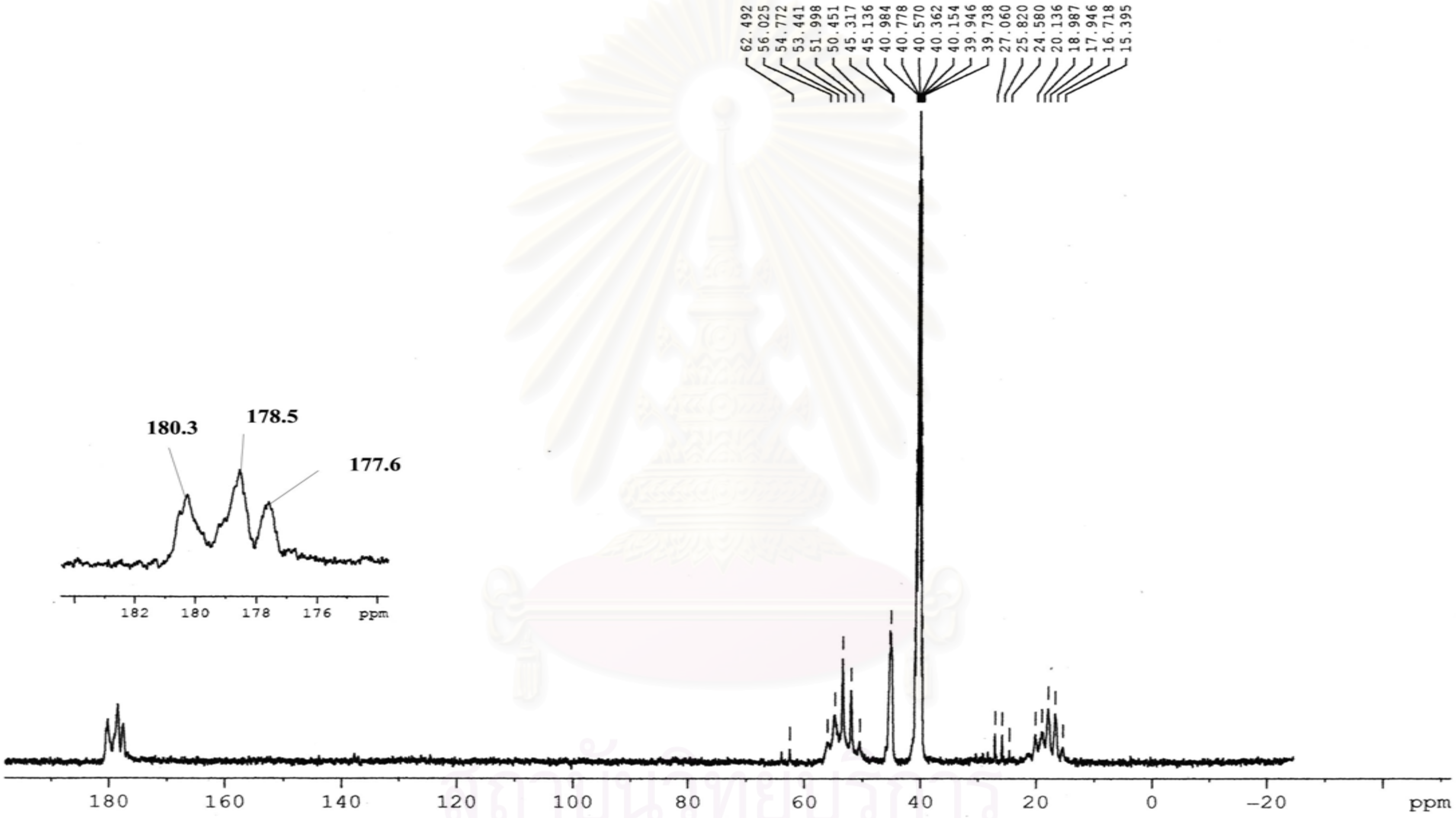


Figure 4.10 The ^{13}C-NMR spectrum of copolymer of methyl methacrylate and methacrylic acid.

4.1.4 The Selection of the Polymeric Binder [51, 52]

Rigid and hard or soft and flexible monomers can be copolymerized to form the polymer backbone. The effects of different monomers on resulting film properties are very important; in this research we chose methyl methacrylate and methacrylic acid. Methyl methacrylate (MMA) tends to give films with good exterior durability, hardness, stain and water resistance. Methacrylic acid (MAA) tends to give films with good hardness, solvent and grease resistance. Methyl methacrylate (MMA) and methacrylic acid (MAA) copolymers are widely used as filmforming materials, binders in the production of paints and varnishes. Then we used these synthetic copolymers to be the prepolymer or binder of the formulation for UV coating on the aluminium substrate[51].

The method of preparation of a polymer can have a major influence on its properties. Melting, boiling and sublimination are the three changes of state, which are known as first order transition. Second order transitions generally involve changes in the solid state. The energy changes involved are smaller than the latent heats of first order transitions. In polymer physics, the glass transition temperture (Tg) is the most important property of the second order changes and it represents the change from a glass-like-state to a rubber like state. Above the Tg, a polymer is flexible and has a high elongation at break in direct contrast to the brittle glass form which exists below the Tg. The Tg is directly influenced by the proportion of a monomer in the polymer[52]. In this case, the Tg of a MMA homopolymer is 115°C and and for a MAA homopolymer is 230°C. Thus, a copolymer formed from MMA and MAA will have a Tg between 115°C and 230 °C, depending on the relative proportion of each monomer.

For soft tacky films a low Tg or a selection of low Tg co-monomers would be used and in contrast for hard brittle films. However, most films require a compromise of properties and these can be obtained by copolymerizing more than one type of monomer[51].

The mechanical properties required from a cured coating include hardness, flexibility, adhesion, abrasion resistance, strength, durability, scratch resistance and toughness. Many of these properties are inter-related and primarily depend on the following[52]:

i) the chemical structure of the prepolymer
ii) the molecular weight of the prepolymer.
iii) the functionality of the diluent
iv) the nature of the crosslinked network

The hardness of a coating is enhanced by increasing the crosslink density of the cured film. Increasing the functionality of the reactive diluents is the easiest way to achieve this. The use of a prepolymer with components, which have high glass transition temperatures, also helps enhance film hardness. The more rigid the prepolymer and the more rigid the crosslinking, the harder the cured film. Flexibility is improved with decreasing crosslink density. Thus, the use of monofunctional diluents or prepolymers with high molecular weights per acrylate functional group improves flexibility. The structure of the prepolymers can influence flexibility significantly. The addition of inert resins may improve the flexibility of the cured film by reducing the crosslink density. However, the structure (Tg) of the inert resin and the amount incorporated into the formulation will have a significant effect on the resulting properties. Using a low Tg resin at levels greater than 10% will improve the flexibility of a cured formulation, but again the resistance properties may suffer.

Photoinduced degradation can occur through light, particularly UV; thereby causing polymer chains to fragment. Interactions can then occur with oxygen in the air giving peroxy radicals. These radicals can interact with other sites within the polymer network and form another crosslink or they can form hydroperoxides, which possibly undergo further reactions causing chain scission and a breakdown in the properties of the cured film. The high crosslink densities of UV cured films limit their photodegradation compared to a conventional film, because the radicals which are formed have very limited mobility. However, residual photoinitiator can be activated by incident radiation and can again generate radicals. The photoageing of a radiation cured film depends on the degree of cure, the functionality of the monomer, the chemical structure of the prepolymer and the type and amount of residual photoinitiator. The greater the functionality of the monomer, the higher the crosslink density, and the lower the extent of photodegradation. Conversely a highly funtionalised monomer can give rise to a significant number of entrapped unreacted double bonds. This is obviously detrimental to the weathering performance of the film. Prepolymer containing aromatic groups are less stable towards photoageing than their corresponding aliphatic prepolymers[52].

Thus, in this research we chose the copolymer binder T16 with the high molecular weight (128,000) and moderate Tg (163.4°C) when comparing with other copolymers synthesized to be the suitable prepolymer for the formulation.

4.2 The Quality of the Printing Plate

Platemaking is the important process because printing plate is used for transfering image from an original film or imagewise to paper. When making a lithographic plates, we have to ensure some basic objectives as summarized below:

- Images should be correctly and accurately positioned relative to other images and plate itself.
- Imaging and processing should ensure and enhance the difference in wetting between image and non-image areas.
- Nonprinting areas should be well desensitized and free from marks and unwanted image.
- Ensure that maximum plate life is possible.

All of these properties relate to the functionality of the plate in the lithographic process, but it is apparent that the control of dot gain in printing is intricately tied to the control of image transfer in platemaking. Fortunately, modern presensitized plates are quality controlled during manufacture and imaging is relatively easy to control with the aid of some simple control devices[9], that is UGRA plate control wedge.

4.2.1 Photopolymerization of Compositions Possessing Vinyl Unsaturation

Typical recipes of the photosensitive material were prepared by the formulation as given in Table 4.8

Table 4.8 Formulation of photosensitive materials for the printing plate.

Photosensitive Materials[a]	**% By Weight**
Binder(copolymer 30% in IPA:MEK 1:1)	58.3
TPGDA	21.0
TMPEOTA	12.2
Darocur 1173	4.3
Darocur BP	3.9
Pigment	0.3
Total	100.0

[a] viscosity is 4.4 Pa s at shear rate 8 sec^{-1} and shear stress 35 dyne/cm^2 , by Brookfield viscometer (model RVT) at 25°C.

The photosensitive coating was coated onto an anodized aluminium substrate by spin coating, which formed a smooth, thin film that was overcoated by a 2% PVA solution for preventing the inhibition of oxygen gas from the air. A control step wedge (UGRA) was assembled with a original separation. In this study we used both negative and positive original UGRA-like plate control wedge.

Then the coated aluminium substrate was exposed to UV radiation at different exposure times for determining an appropriate exposure. The exposed plate was developed in various developers: acetic acid and aqueous base developer to find the most suitable developer.

According to the formulation of UV coating as shown in Table 4.8, the UV chemistry comprises the following materials:

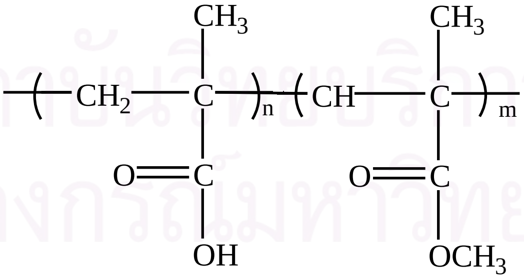
1. Prepolymer or binder : Poly(methyl methacrylate-*co*-methacrylic acid)
2. Reactive diluents : Tripropylene glycol diacrylate (TPGDA) and Trimethylol propane ethoxylate triacrylate (TMPEOTA)
3. Photoinitiator : Darocur 1173 and Darocur BP
4. Additives : Pigment (Phthalocyanine or Anthraquinone)

4.2.1.1 Prepolymer

In this study, we used copolymer of methyl methacrylate (MMA) and methacrylic acid (MAA) as the polymeric binder. Their structures are shown in Figures 4.11 I and II, respectively. The structure of the copolymer of MMA and MAA are also shown in Figure 4.11 III.

$H_2C=C(CH_3)-C(=O)-O-CH_3$ $H_2C=C(CH_3)-C(=O)-O-H$

I. MMA **II. MAA**



$-(CH_2-C(CH_3)(COOH))_n-(CH-C(CH_3)(COOCH_3))_m-$

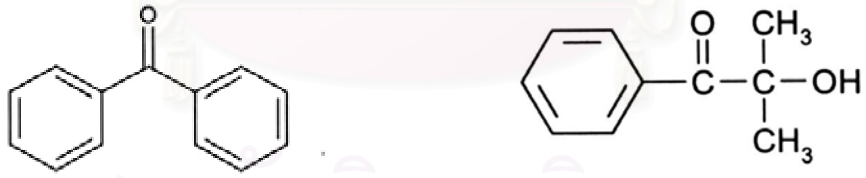
III. P(MMA-MAA)

Figure 4.11 The monomer and copolymer of MMA and MAA.

A photosensitive material has been made by converting a base soluble polymer, such as poly(methyl methacrylate-*co*-methacrylic acid) P(MMA-MAA), that has negligible absorption for radiation of wavelength longer than 230 nm, to a base insoluble polymer [53]. The methacrylic acid has π bonds to make them highly reactive and easy to polymerize or copolymerize with other monomers [3]. Basically methyl methacrylate can be readily polymerized in the presence of UV-radiation both with and without aid of initiators, making them of primary importance in UV curing [6].

4.2.1.2 Photoinitiator

These monomers have unsaturated double bonds that are sensitive to UV radiation. The photopolymerization can occur by photoinitiators Darocur BP and Darocur 1173. Their structure are shown in Figure 4.12 I and II



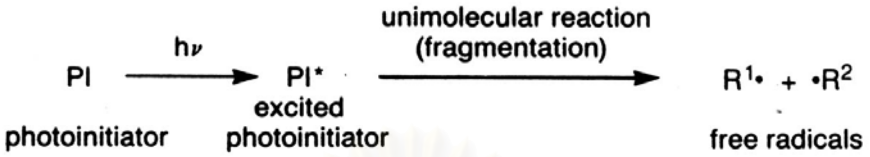
I. Darocur BP **II. Darocur 1173**

(Benzophenone or BP) (2-Hydroxy-2-methyl-1-phenyl-propan-1-one

or 2-Hydroxy-2-methylpropiophenone or HIPK)

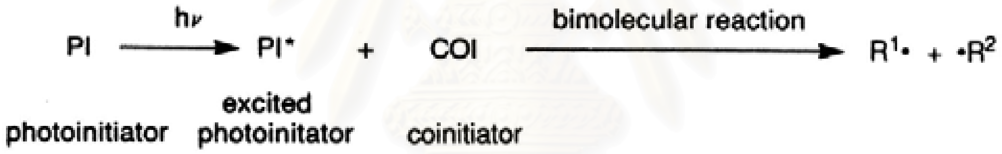
Figure 4.12 The photoinitiator.

Photoinitiators are generally divided in two classes according to the process by which the initiating radicals are formed. The compounds which undergo unimolecular bond cleavage upon irradiation as shown in the following equation is termed Type I photoinitiators or PI$_1$-type initiators [54]:



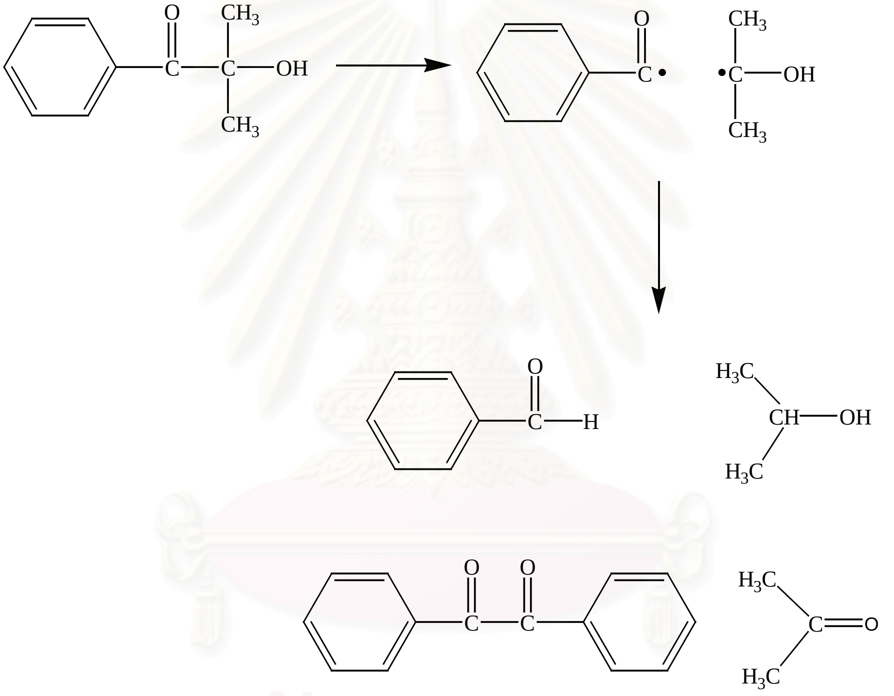
(4.1)

If the excited state photoinitiator interacts with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction as shown in the following equation, the initiating system is termed Type II photoinitiators or PI$_2$-type initiators [54]:



(4.2)

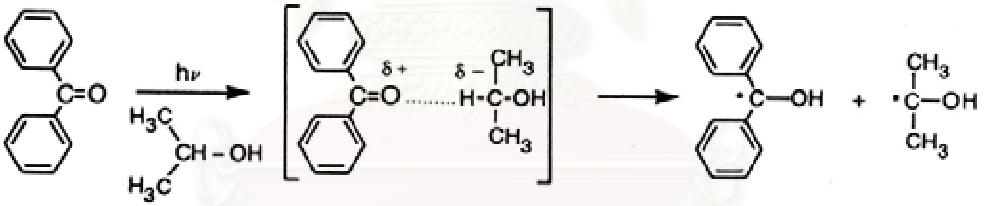
Darocur 1173 or HIPK is the Type I photoinitiator. The majority of Type I photoinitiators are aromatic carbonyl compounds containing suitable substituents which facilitate direct photofragmentation, thereby producing radicals. The aromatic carbonyl moiety acts as the chromophore group. Depending on the nature of the functional group and its location in the molecule relative to the carbonyl group, the fragmentation can take place at a bond adjacent to the carbonyl group (α-cleavage), at a bond in the β-position (β-cleavage). By far the most important fragmentation in photoinitiator molecule is the absence of any aromatic substituent in the hydroxy alkyl moiety, which prevents the α-cleavage of the carbon-carbon bond between the carbonyl group and the alkyl residue in the alkyl aryl ketones which is known as the Norrish Type I reaction[54]. HIPK has the absence of aromatic substituent in the hydroxy alkyl moiety prevents the formation of chromophoric compounds, thus non-yellowing, clear acrylic coating can be achieved. The photochemistry shows that Norrish Type I α-cleavage in Figure 4.13 (equation 4.3) is the main decay of the excited species and that, before escape, an important fraction of the radical pair reacts in the cage leading to carbonyl-type rearrangement products [55].



(4.3)

Figure 4.13 The photolysis pathway of HIPK [55].

HIPK is the most diffuse non-yellowing photoinitiator, gives rise upon irradiation, both to benzaldehyde and to acetone and cyclohexanone, respectively, in some cases even in the presence of monomers or oligomers, leading to coatings with odour problem. A possible solution for the odour problem can arise from the use of polymeric photoinitiators that is HIPK and BP (whose efficiency cannot compare with that of the α-cleavage type) [55]. There are the two main reaction pathways available for Type II photoinitiator (BP); hydrogen abstraction by the excited initiator and photoinduced electron transfer, followed by fragmentation. A typical hydrogen abstraction process is the reaction of excited ketones with hydrogen donors, such as alcohols. Upon excitation of the ketone to its $n\pi^*$ triplet state, an electron is promoted from the non-bonding n orbital on oxygen to an antibonding π orbital which is delocalised over the aromatic π system, thus rendering the excited state oxygen more electrophilic. The partial positive charge on oxygen can then interact with the electron rich C–H bond adjacent to the heteroatom resulting in hydrogen abstraction. This is shown in Figure 4.14 (equation 4.4) for the benzophenone-isopropanol couple [54].



(4.4)

Figure 4.14 Photoreduction of benzophenone by isopropanol [54].

Combinations of HIPK (Type I photoinitiator) and BP (Type II photoinitiator) are superior to either alone for UV curing in air. The Type I photoinitiator (HIPK) is believed to furnish the primary radicals which deplete the oxygen in the system. The Type II photoinitiator (BP) possibly induces the photosensitized decomposition of the hydroperoxide formed. Both photoinitiators contribute to the initiation of polymerization via their corresponding initiation mechanisms. Therefore, in practice mixtures of photoinitiators are often used in order to exploit this and other synergistic effects [55].

Photoinitiators of Darocur 1173 (HIPK) and Darocur BP (BP) are present in photopolymerizable systems to initiate the polymerization reaction. They are light-sensitive compounds, which absorb radiation energy and give rise to the formation of the primary free radicals, which can initiate the chain propagation reaction by reacting with the unsaturations present in the systems[31].

As the polymerization proceeds, the viscosity of the irradiated medium increases steadily to yield a solid, highly cross-linked polymer in which the segmental mobility is severely restricted. The reaction proceeds further in this phase, although the encounter probability of the polymer radicals with the unreacted acrylate double bonds is sharply reduced until all the mobile and accessible reactive groups have been consumed and an insoluble network has been formed.

The overall reaction scheme of the photopolymerization of a monomer, *M*, in the presence of a photoinitiator of a radical, *I*, may be represented by the following set of equations [5];

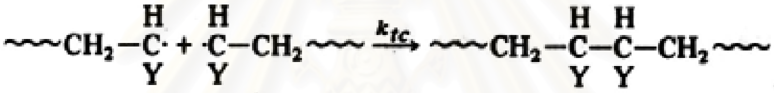
Activation by UV radiation: $$PI + h\nu \longrightarrow PI^* \qquad (4.5)$$

Initiation: $$I^* \longrightarrow 2R^{\bullet} \qquad (4.6)$$

Propagation: $$R^{\bullet} + M \longrightarrow M_1^{\bullet} \longrightarrow P^{\bullet} \qquad (4.7)$$

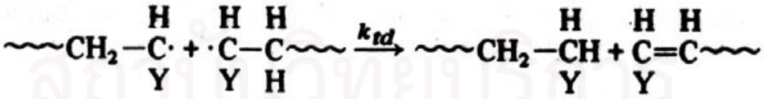
Termination: $P^{\bullet} + P^{\bullet} \longrightarrow \textit{Polymer}$ (4.8)

The photoinitiator was activated by the UV radiation, then move from the ground state to excited state. The rate of reaction of a radical with a monomer molecule is independent of the particular type of radical and its chain length. The termination step has two ways to proceed. First, termination with the annihilation of the radical centers occurs by bimolecular reaction between radicals. Two radicals react with each other by *combination* (coupling) [5]:



$$\sim\sim\sim CH_2-\underset{Y}{\overset{H}{C}}\cdot + \cdot\underset{Y}{\overset{H}{C}}-CH_2\sim\sim\sim \xrightarrow{k_{tc}} \sim\sim\sim CH_2-\underset{Y}{\overset{H}{C}}-\underset{Y}{\overset{H}{C}}-CH_2\sim\sim\sim \tag{4.9}$$

Second, termination by *disproportionation* in which a hydrogen radical that is *beta* to one radical center is transferred to another radical center. This results in the formation of two polymer molecules–one saturated and one unsaturated [5]:



$$\sim\sim\sim CH_2-\underset{Y}{\overset{H}{C}}\cdot + \cdot\underset{Y}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\sim\sim\sim \xrightarrow{k_{td}} \sim\sim\sim CH_2-\underset{Y}{\overset{H}{CH}} + \underset{Y}{\overset{H}{C}}=\overset{H}{C}\sim\sim\sim \tag{4.10}$$

Termination can also occur by a combination of coupling and disproportionation. The two different modes of termination are very important. Both MMA and MAA monomers contain beta hydrogen atoms and thus both termination modes have been observed. The polymeric binder, MMA and MAA monomers undergoes the greater disproportionation as shown in Table 4.9.

Table 4.9 The termination of free radical polymerization at 60°C [56].

Monomer	Formulation	Percent of termination	
		Disproportionation	Combination
MMA	$CH_2=C(CH_3)–COOCH_3$	79	21
MAA	$CH_2=C(CH_3)–COOOH$	<79[a]	>21[a]

[a] approximated values

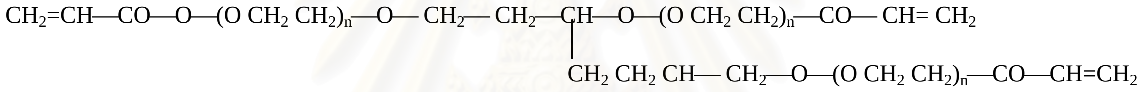
Table 4.9 indicates that the monomer polymerization of MMA and MAA can be terminated by disproportionation more than combination. Their percentage termination by disproportionation of MMA is more than MAA because of the beta hydrogen atoms and the steric hindrance of methyl group. Both MMA and MAA monomers have the β-hydrogen that can transfer to another radical center.

4.2.1.3 Reactive Diluents

Monomers or reactive diluents include different compounds, which are present in the radiation-curable systems performing the primary function of fluidizing agents and viscosity-control agents. Moreover they act as cross-linking agents, to increase or decrease the cross-linking density in the polymer network, modifying the final product properties. Due to the fact that the monomers participate in the curing process by copolymerizing with the unsaturations present in the oligomers or prepolymer, they have a great influence either on the cure kinetics and photoresponse rate or on the properties of the coating–mainly mechanical properties, film hardness, flexibility, chemical resistance and adhesion. The molar concentration of the monomers in the system determines its influence on the film properties [57]. Too high a monomer concentration often decreases the film’s mechanical properties, therefore for any system there is an optimum monomer/oligomer ratio in order to have the best film characteristics[31]. In this study we used the low irritancy oligomer or multifunctional monomers such as TPGDA and TMPEOTA. Their structures are shown in Figures 4.15 I and II.

$$CH_2{=}CH-CO-O-(CH_2\,CH_2\,CH_2O)_3-CO-O-CH{=}CH_2$$

I. TPGDA



$$\begin{aligned}&CH_2{=}CH-CO-O-(O\,CH_2\,CH_2)_n-O-CH_2-CH_2-\underset{\displaystyle |}{C}H-O-(O\,CH_2\,CH_2)_n-CO-CH{=}CH_2\\&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2\,CH_2\,CH-CH_2-O-(O\,CH_2\,CH_2)_n-CO-CH{=}CH_2\end{aligned}$$

II. TMPEOTA

Figure 4.15 The structure of reactive diluents or monomers[58].

With multifunctional monomers, the understanding of the reaction mechanism is complicated by the fact that unreacted groups may be present either in free monomer or as pendant groups. Initially, the pendant bonds appear to exhibit enhanced reactivity with respect to free monomer. Pendant double bonds become much less mobile than the free monomer. As the monomer functionality increases the polymerization was shown to develop faster, due to a higher initial concentration of reactive group, but to stop earlier owing to gelification, which limits the extent of the polymerization process, thus leading to the cross-linked polymer that contains a substantial amount of unreacted double bonds. The room-temperature photopolymerization of multifunctional acrylates usually leads to glassy polymers in which only part of the available double bonds are reacted. Upon polymerization the system passes through the glass transition isothermally and so the mobility of the unreacted double bonds is strongly reduced. Nevertheless, diffusion of free monomer is still at work as well as transport of reactive sites via chain transfer for the reduced reaction rate, as with increasing segmental mobility restrictions, the radical pairs generated by the photocleavage of the photoinitiator have more tendency to recombine than to diffuse apart and initiate new polymer chain. The rate constants (k_p and k_t) of MMA and MAA are shown in Table 4.10

Table 4.10 The comparison of reactivity by rate constants of MMA and MAA[56].

Monomers	**k_p^a (M^{-1} s^{-1})**	**k_t^b (M^{-1} s^{-1})**	**$k_p/k_t^{1/2}$ $(M^{-1}$ $s^{-1})^{1/2}$**
MMA	705	1.8	390
MAA	670	2.1	320

[a] k_p = rate constant of propagation reaction.

[b] k_t = rate constant of termination reaction.

The reactivity ratios for monomer MMA (r_1) and MAA (r_2) are 0.78 and 0.33, respectively. Based on the $k_p/k_t^{1/2}$ ratio between MMA and MAA, more MMA units are added in the polymer chains. The high molecular weights of the copolymer could be obtained because the ratios of $k_p/k_t^{1/2}$ are relatively high. This observation is also confirmed by the monomer reactivity. The greater reactivity of MMA results in its being incorporated preferrentially in the first-formed copolymer. As the reaction proceeds the feed and therefore the copolymer become progressively enriched in MAA, because MMA has been used up earlier.

Because the termination mode of both MMA and MAA monomers favor disproportionation, most of the copolymer chains terminate to produce an unsaturation of methacrylate moiety at the chain end which is more sensitive to UV radiation than the acid moiety. In the curing reaction, the exposed polymeric binder can still further polymerize with itself or the reactive monomers. Any overexposure should be avoided because dot gain in the negative-working plate could be enormously high.

In the negative working system (see Figure 4.16), ultraviolet radiation causes the photopolymer coating to crosslink and harden. The plate coating is exposed through a photographic negative (screened in the case of half-tone images), and the clear areas on the negative transmit UV radiation to the reactive surface coating of the plate. The dark areas on the negative represent those reflecting light in the original, that is the screened mid-tone and highlight areas(white), whereas the clear regions correspond to darker or shadow tones. For black text on white paper, the negative produced would comprise dark areas corresponding to the white paper, and clear areas corresponding to the text. When printed down onto the negative working plate surface, UV radiation passes through the clear, (text) areas producing a light-hardened ink-receptive image of the text on the printing plate (the contrast or gamma of graphic arts litho film is very high, 14 or more. Hence light from original copy is only recorded above a specific intensity threshold, resulting in either a black silver image or clear film.)

The coating applied to negative working plates falls into three categories, defined by their action:

- Photoinsolubilization
- Photopolymerization
- Photocrosslinking

In all three processes a solubility differential is set up between the exposed and unexposed areas of the coating, and the plate is developed using water, aqueous alkali or solvent. Environmental requirements have led to great interest in aqueous developers [57].

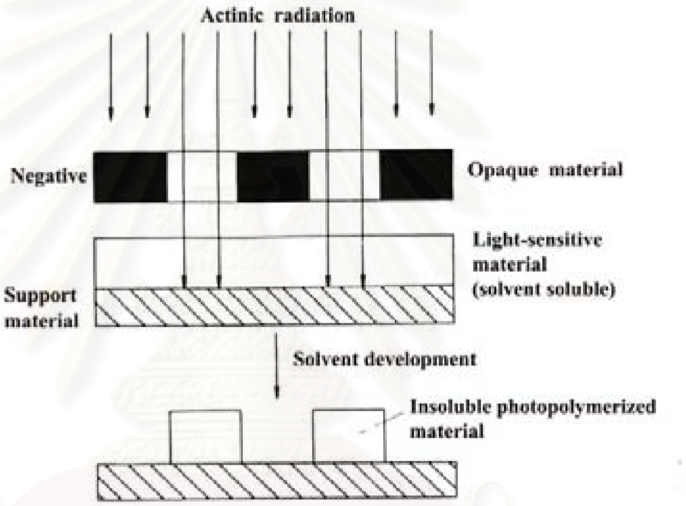


Figure 4.16 The negative working plate [7].

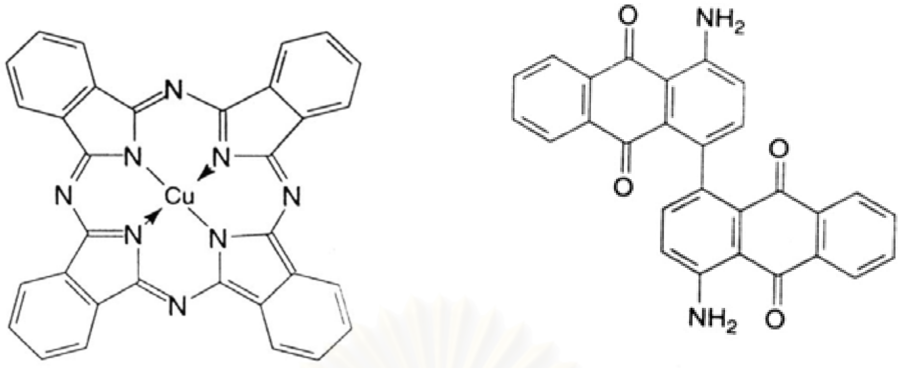
4.2.2 Effect of Pigment on Visibility on the Plate

From the photosensitive material prepared by the formulation as given in Table 4.8, the image formed on the plate cannot be easily viewed. A suitable pigment, which does not interfere the working conditions of the ingredients, should be added to enhance the contrast between the image and non-image areas. The images on the resulting plates were made clearly visible by two types of pigments to find the most suitable pigments incorporated in the UV-sensitive material. The result is shown in Table 4.11

Table 4.11 The effect of pigment on the image appearance.

Pigment	Resulting image on plate	
	Negative plate	**Positive plate**
Phthalocyanine (Ciba® **ORACET®** Blue G)	Phase separation	phase separation
Anthraquinone (Ciba® **ORACET®** Red BG)	compatible	phase separation

Table 4.11 indicates that phthalocyanine is not suitable for this photosensitive material for UV irradiation, because the image could not be viewed on both negative and positive working plates. On the other hand, anthraquinone is the most suitable pigment for using in this photosensitive material formulation for UV irradiation. The resulting image was obtained on the negative working plate only. The structure of phthalocyanine and anthraquinone are shown in Figure 4.17 I and II, respectively.



I. **II.**

Figure 4.17 The phthalocyanine blue (left) and anthraquinone (right) pigment[59].

It seems that phthalocyanine blue pigment does not well mix with the binder system, flocculation occurs and phase separation is the main reason for curing. On the other hand, anthraquinone is very compatible with the base polymer and other ingredients in the coating formulation. This phenomena can be observed because of pigment structures as shown in Figures 4.17 I and II. Copper phthalocyanine is the metal complex pigment which is non-polar, but anthraquinone is relatively polar, because of the amine group like our polymeric binder, so anthraquinone is more compatible with the coating than phthalocyanine. This pigment (anthraquinone) enables the coating to perform their function well because the image and non-image areas are easy to view.

4.2.3 Effect of Developer

After the photosensitive solution or coating in Table 4.8 was coated onto an anodized aluminium substrate by spin coating, and overcoating with a 2% PVA solution as an oxygen barrier, then the photosensitive material coated aluminium substrate was exposed to UV radiation. At last the exposed plate was developed, either by 10% acetic acid or Fuji Film Developer DN-3C. The result of the development is shown in Table 4.11.

Table 4.12 The effect of developer on the images on printing plate.

Developer	**Resulting Image on plate**	
	Negative plate	**Positive plate**
10% Acetic acid	×[a]	×
Fuji Film Developer[c] (aqueous-base developer)	✓[b]	×

[a] × = the image could not be viewed.

[b] ✓ = the image could be viewed.

[c] dilution: 1 parts of the developer with 5 parts of water.

Table 4.12 indicates that 10% acetic acid (organic solvent) is not a suitable developer for this type of printing plate because the latent image could not be developed on both negative and positive working types. The acid-acid interaction could not be possibly observed based on the rules of thumb "like dissolves like". Since Fuji developer DN-3C is an alkaline developer containing the major ingredient of organic compounds dissolved in aqueous sodium hydroxide. The solubility of the coating and developer chemistry are the attributes of "acid-base interaction". The crosslinked areas cause changes in solubility (less or insoluble), which remain as is during development. This is the so called photocrosslinking and photoinsolubilization. Fuji Film Developer DN-3C (aqueous developer) is the suitable developer for this type of plate chemistry because it dissolves the unexposed, non-image areas, while the exposed, image areas remains unchanged. The resulting image was seen on the negative working plate only.

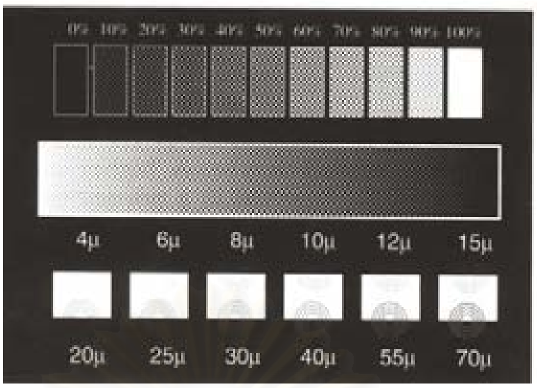
4.2.4 Determination of Exposure Condition

To determine the appropriate exposure condition, we studied the percentage dot areas between the original film (UGRA-like plate control wedge) as shown in Figure 4.18 and the reproduction at 40, 50 and 60%.

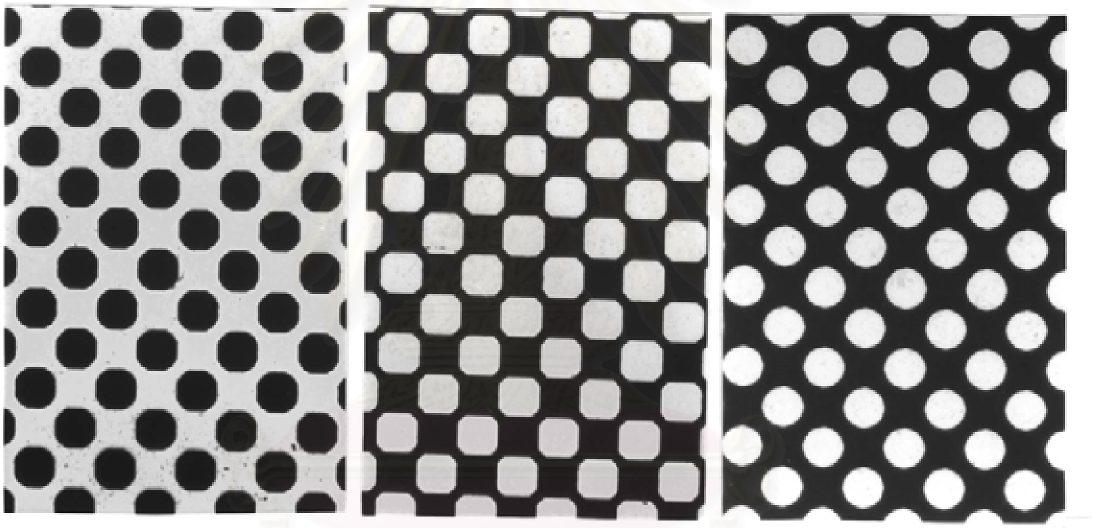
4.2.4.1 Effect of Exposure Time On Dot Reproduction

The amount of light to which the plate is exposed is the principal variable that the platemaker has to adjust in order to control the image transfer to plate. It is also the most significant factor affecting the basic plate requirements that have been explained in the early Section. All plates need a sufficient level of exposure in order to make the required changes to take place in the coating, so that a proper differential between image and non-image is accomplished and an acceptable plate life is achieved[10].

In this study, we investigated the relation of %dot area at 40, 50 and 60% between the original film and the reproduction viewed and measured by an Image Analyzer (Lusex-F software Programme of Nireco QJ 8500:Olympus SZH10). The %dot area values of the resulting plate prepared by varying the exposure times and different copolymer binders (T05, T13, T16, T24) and the monomer ratios (T16-80, T16-70, T16-50) are shown in Figure 4.19. The dot appearance of the above-mentioned parameters is illustrated in Figures 4.20a to 4.20d.



(a.)

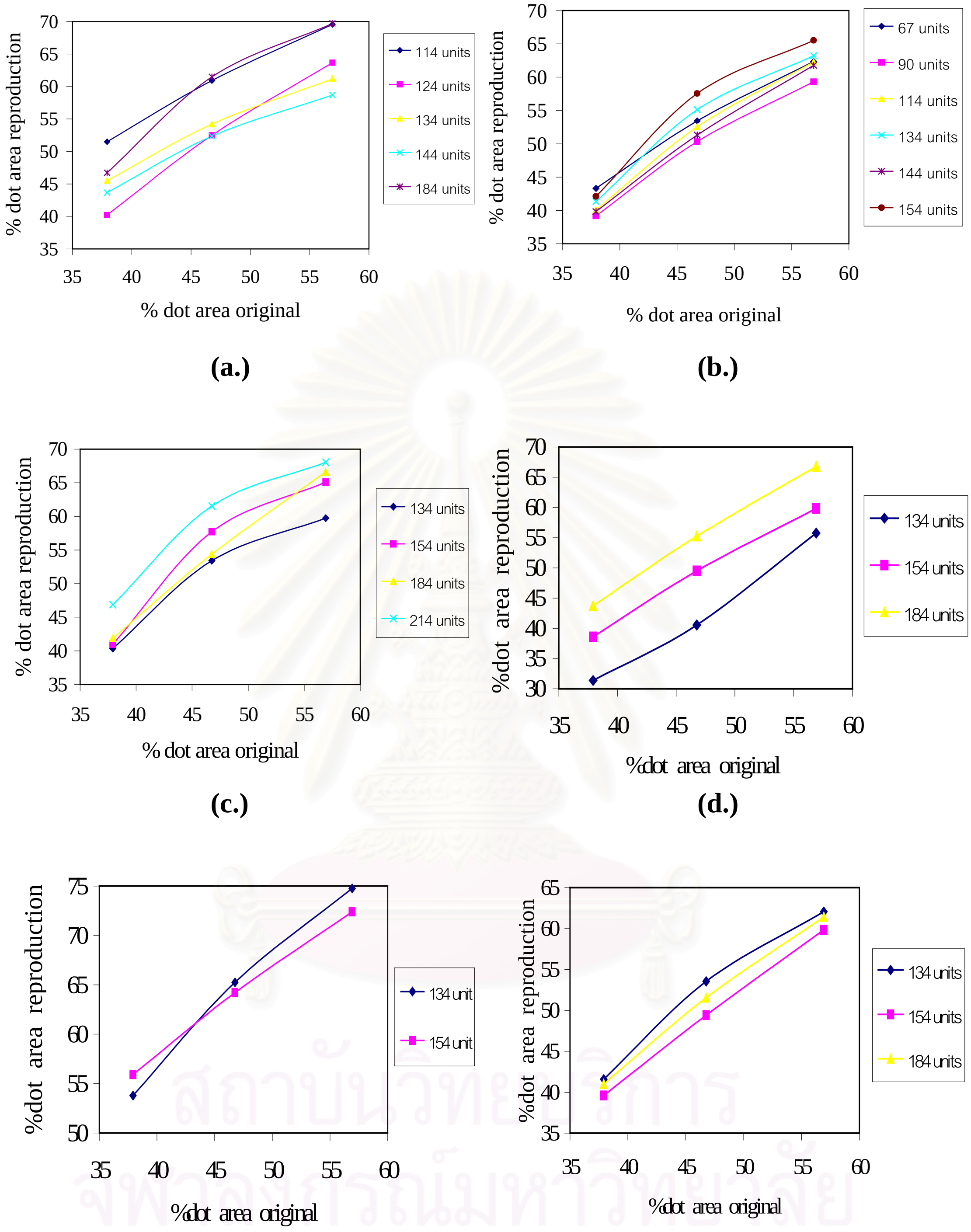


40% **50%** **60%**

(b.)

Figure 4.18 (a.) Top center, negative film control wedge, UGRA-like plate.

(b.) Bottom left, 40% squared dot; bottom center, 50% squared dot; and bottom right, 60% round dot.



(a.) **(b.)**

(c.) **(d.)**

(e.) **(f.)**

Figure 4.19 Relationship between %dot area of the original film and the reproduction of the negative plate prepared by various copolymer binders at a function of exposure time: (a.) T05, (b.) T13, (c.) T16-70, (d.) T16-80, (e.) T16-50 and (f.) T24.

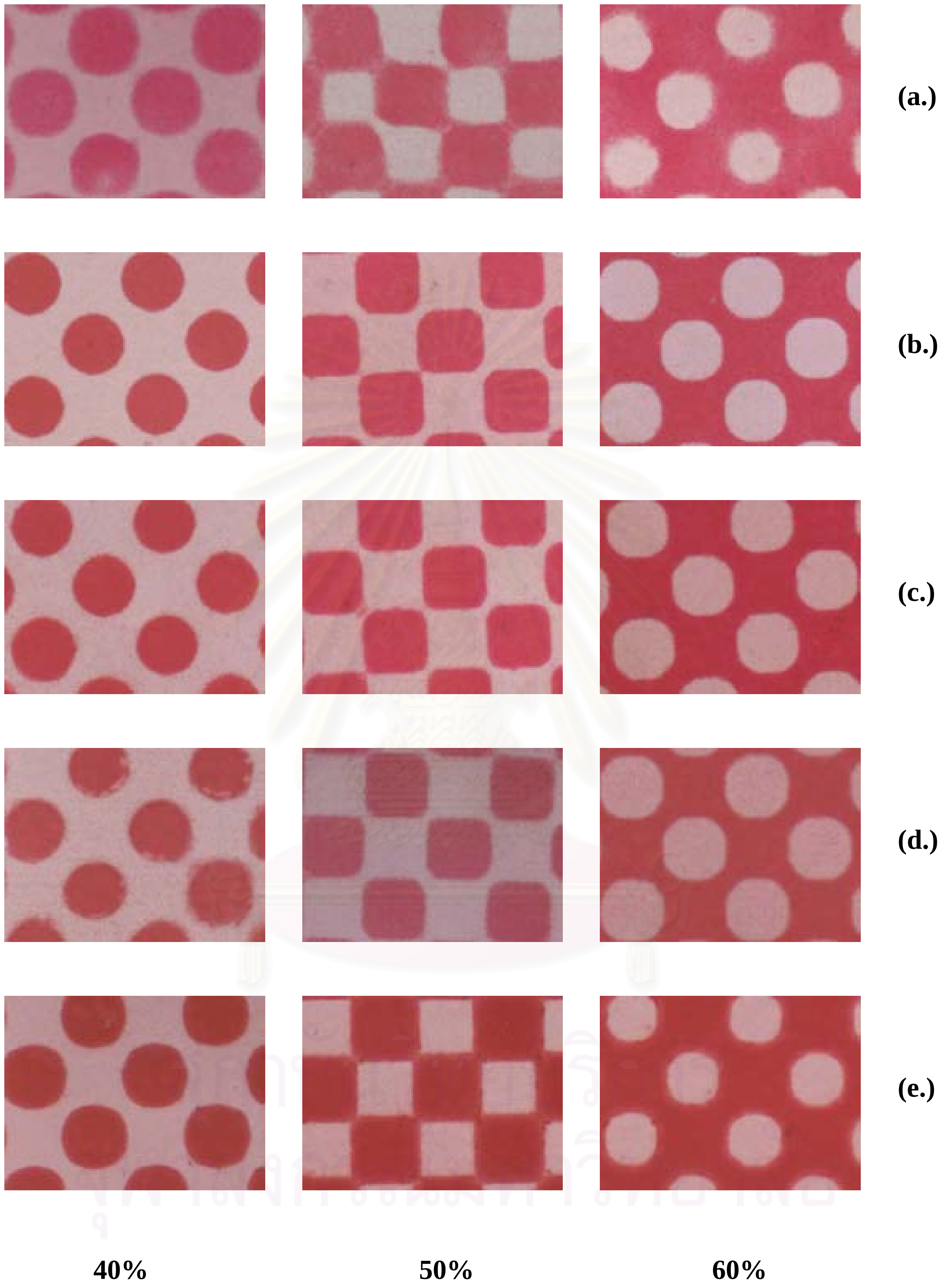


Figure 4.20a Photographs (2X) of %dot area of the reproduction at 40 (all left), 50 (all center), and 60% (all right) of the negative plate prepared from the copolymer binder T05 at various exposure times: (a.) 114 units, (b.) 124 units, (c.) 134 units, (d.) 144 units, and (e.) 154 units.

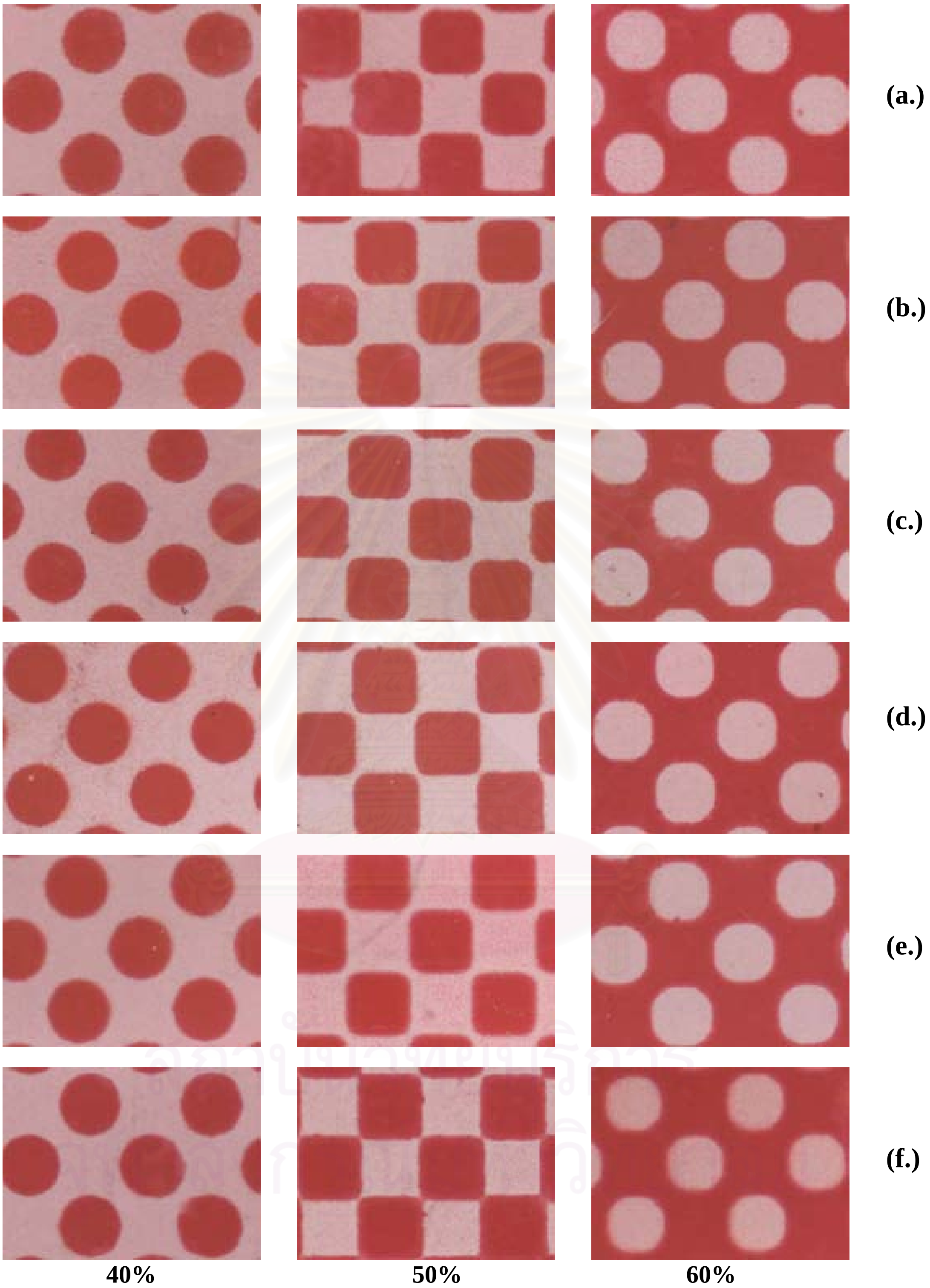


Figure 4.20b Photographs (2X) of %dot area of the reproduction at 40 (all left), 50 (all center), and 60% (all right) of the negative plate prepared from the copolymer binder T13 at various exposure times: (a.) 67 units, (b.) 90 units, (c.) 114 units, (d.) 134 units, (e.) 144 units, and (f.) 154 units.

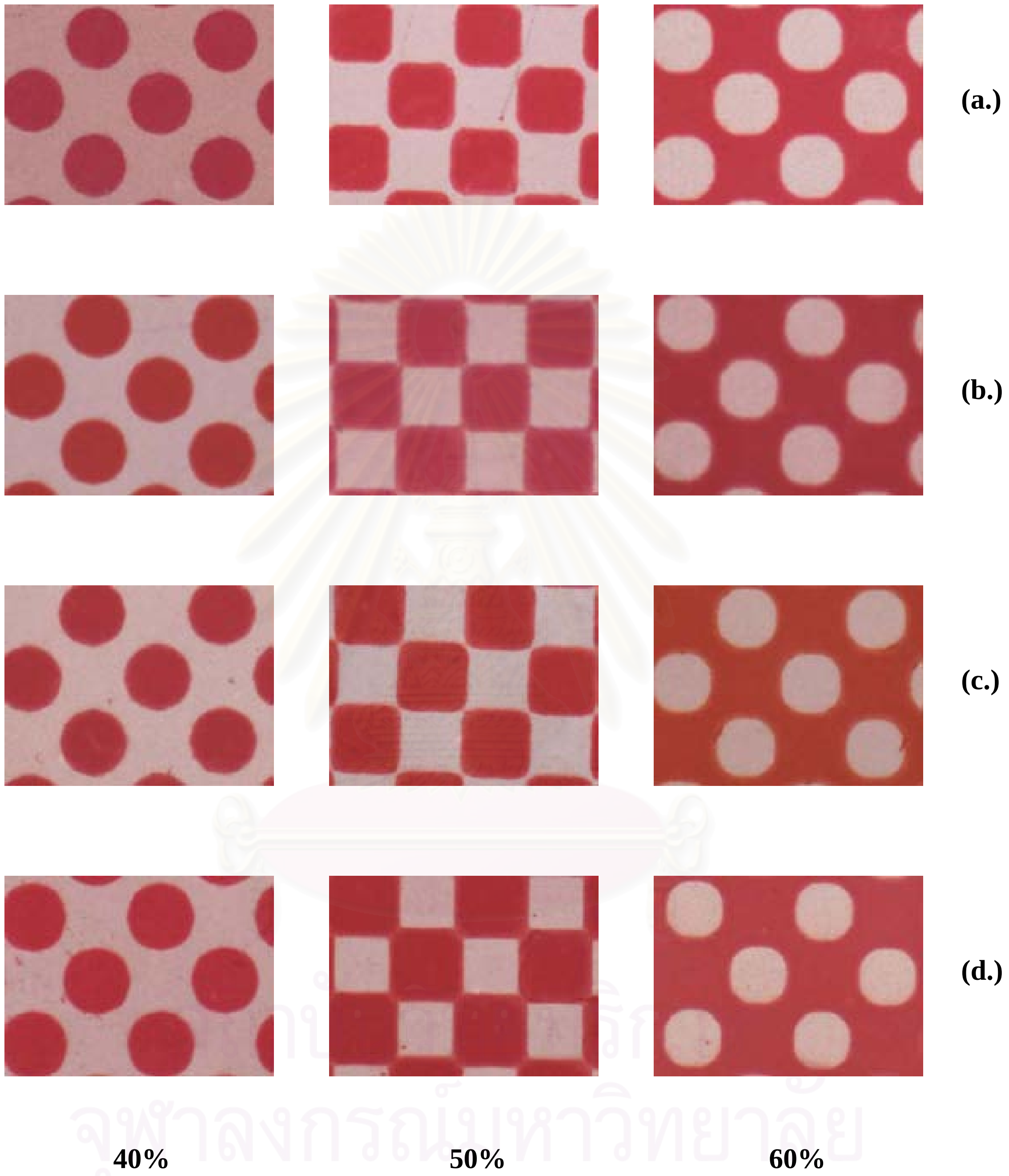


Figure 4.20c Photographs (2X) of %dot area of the reproduction at 40 (all left), 50 (all center), and 60% (all right) of the negative plate prepared from the copolymer binder T16-70 at various exposure times: (a.) 134 units, (b.) 154 units, (c.) 184 units, (d.) 214 units.

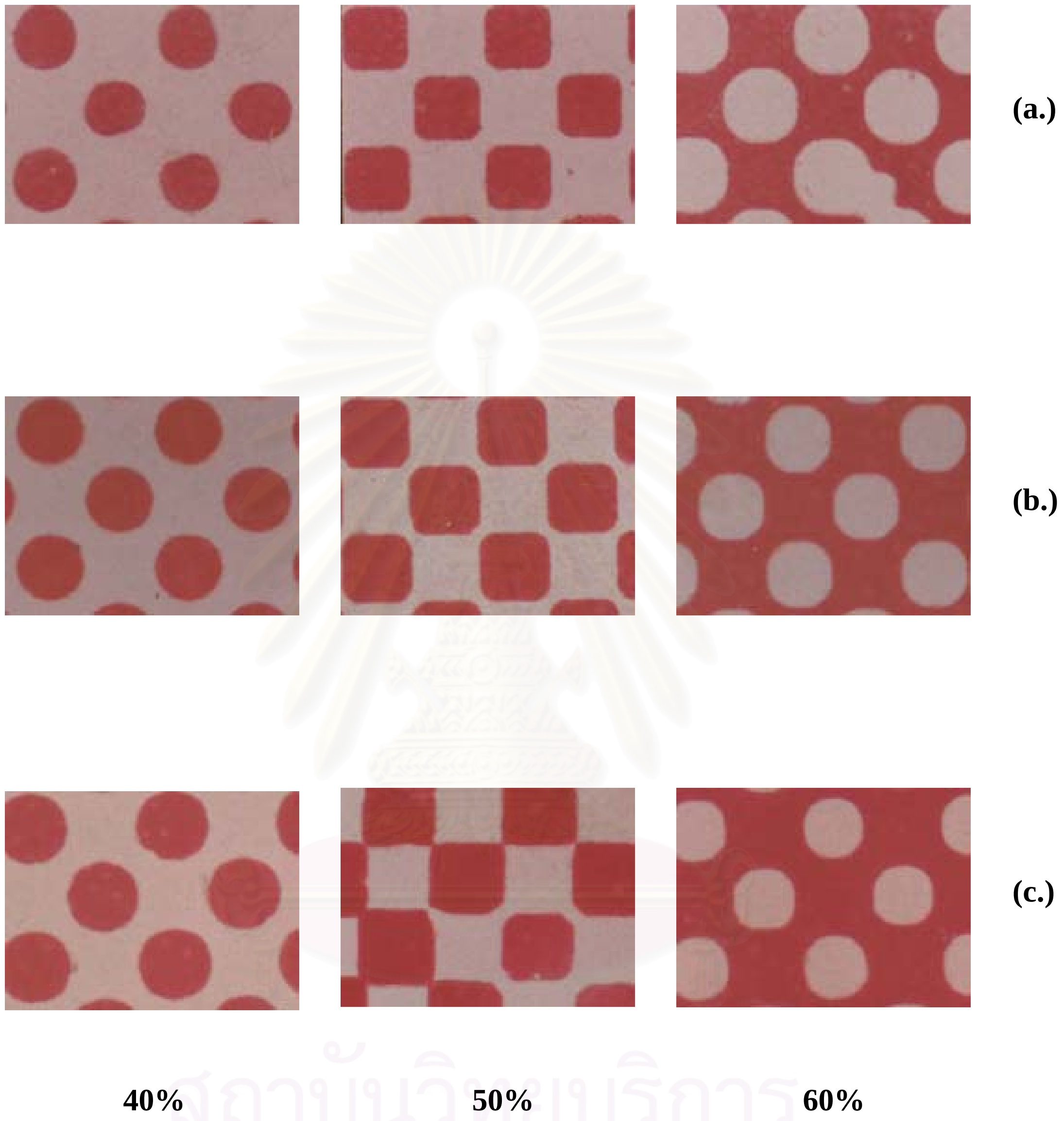


Figure 4.20d Photographs (2X) of %dot area of the reproduction at 40 (all left), 50 (all center), and 60% (all right) of the negative plate prepared from the copolymer binder T16-80 at various exposure times: (a.) 134 units, (b.) 154 units, and (c.) 184 units.

The appropriate exposure time was determined by a relationship of %dot areas at 40, 50 and 60% between original film (UGRA-like plate control wedge) and reproduction as illustrated in Figure 4.19. From these Figure, the best exposure time is the sufficient time that produces the %dot area reproduction with a minimum difference between the original film and the reproduction. The appropriate exposure time for each negative plate prepared from various copolymer binders can be summarized in Table 4.13

Table 4.13 The appropriate exposure time for the negative plate prepared from various copolymer binders.

Runs	***M_w***	***PDI***	**Appropriate exposure time**	
			Units	Sec
T05	78,000	2.1	134	65
T13	79,000	1.9	144	69
T16-70	128,000	1.9	184	89
T16-80	129,000	2.2	154	74
T16-50	132,000	2.1	154	74
T24	70,000	1.9	154	74

Table 4.13 indicates that M_w and PDI affect the UV-sensitivity. When the higher molecular weight polymer was used, the exposure time would tends to be longer.

Increased exposure reduces image sizes on positive working plates, but increases image sizes on negative plates. The correct exposure time for a plate has to be established by the platemaker since it is affected by:

- speed and sensitivity of the plate coating,
- spectral output of the exposing light source,
- distance of light source from the plate,
- density of film and foils.

The intensity of actinic light tends to reduce during the life of the plate exposure lamp and may vary with fluctuation in the power supply. For this reason control of the exposure is greatly improved if its duration is measured by a light integrator rather than a timer. Since we are only concerned with the actinic light to which the plate is sensitive, the light integrator should therefore be filtered to provide this sensitivity.

With some poorly designed exposure units there may be considerable variation in the intensity of actinic light from the outer edge of a plate. This is estimated to be as great as 2 to 1 in some instances. The significance of these differences in terms of controlling image transfer will depend on the film and exposure latitude of the plate being used.

A different type or batch of plate may necessitate different exposure settings to achieve a standard image transfer. It should therefore be normal practice to check each new batch of plates to establish if any change is necessary[9].

4.2.4.2 Effects of the Copolymer Binder, Monomer Ratio and Reaction Time on Polymerization in terms of Dot Reproduction

From the effect of exposure time, we can compare %dot area produced from each suitable exposure time with %dot area of the original film so as to determine the best molecular weight of the polymeric binder and monomer system as shown in Table 4.14

Table 4.14 The comparison of %dot area at appropriate exposure time.

D_o[c]	**D_r**[a] **at any exposure time (units)**[b]					
	T05	T13	T16-70	T16-80	T16-50	T24
	134	144	184	154	154	154
38	40	40	42	40	44	56
47	52	51	54	49	55	64
57	64	62	67	60	67	77

[a] D_r = %Dot area of the reproduction (the resulting plate)

[b] 1 unit = 0.48 sec

[c] D_o = %Dot area of the original film (UGRA-like plate control wedge)

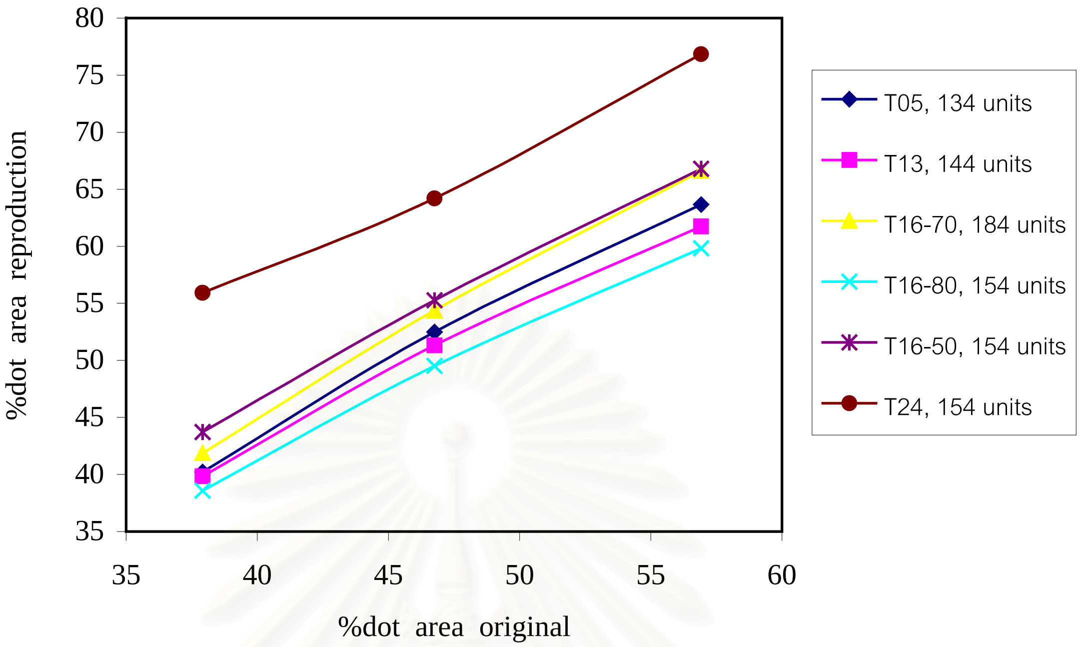


Figure 4.21 The relationship between %dot area of the original film and dot reproduction of the negative plate at the appropriate exposure time of the plate.

Figure 4.21 shows that the suitable copolymer binder is the one that can faithfully produce the dot areas similar to those of dot original, whose tone reproduction should be as close as possible to the 45 angle line through the original (0,0 points). So, the best copolymer binder to prepare the negative printing plate is T16-80 (the copolymer of methyl methacrylate and methacrylic acid synthesized from MMA:MAA of 80:20 for 16 hours). One important property for tone reproduction of half-tone plate is the extent of dot gain around the mid-tone (40-60% dot areas). One can observe clearly that the T16-80 copolymer-monomer system produced the least %dot gains of 0.5% and 0.1% at 46.76 and 56.92 % dot area, respectively. First, the polymerization extent is responsible for the dot reproduction because it produces the crosslinking area when exposed to UV radiation. Second, the lesser extent parameter is the control of alkaline development. The high the alkalinity of the developer as well as the prolonged developing time not only increase the dot area but also the background density. The background density arises from the low extent of polymerization and the acceleration development.

4.2.5 Determination of Optimum Resolution

The optimum resolution is specified as the line width of the lowest step where positive and negative lines are still just visible. The UGRA-like micro-line patch has the line width: 4, 6, 8, 10, 12, 15, 20, 25, 30, 40, 55 and 70 μm A line patch is considered to be reduced to zero or to be a solid-tone, if less than a third of the line is left. The determination of the optimum resolution has to be made on the finished plate, as shown in Table 4.15 and Figure 4.22a to 4.22d.

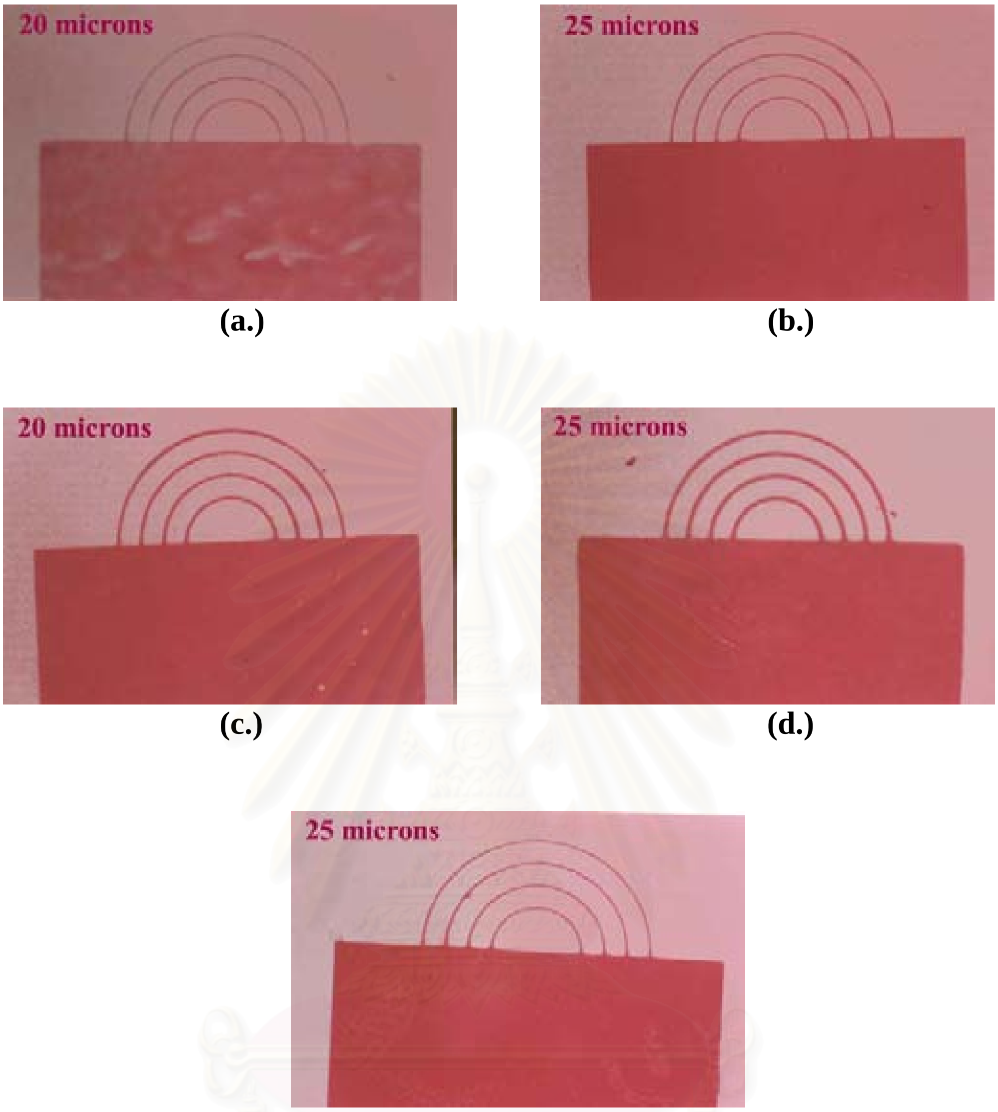
Table 4.15 Exposure time effect on plate resolution.

Runs	Exposure time (units)	Micro-line line width (μm)	
		Beginning point	Perfect point
T05 (M$_w$=78,000 PDI = 2.1)	114	4	20
	124	8	25
	134	6	20
	144	10	25
	184	6	25

Table 4.15 (continue)

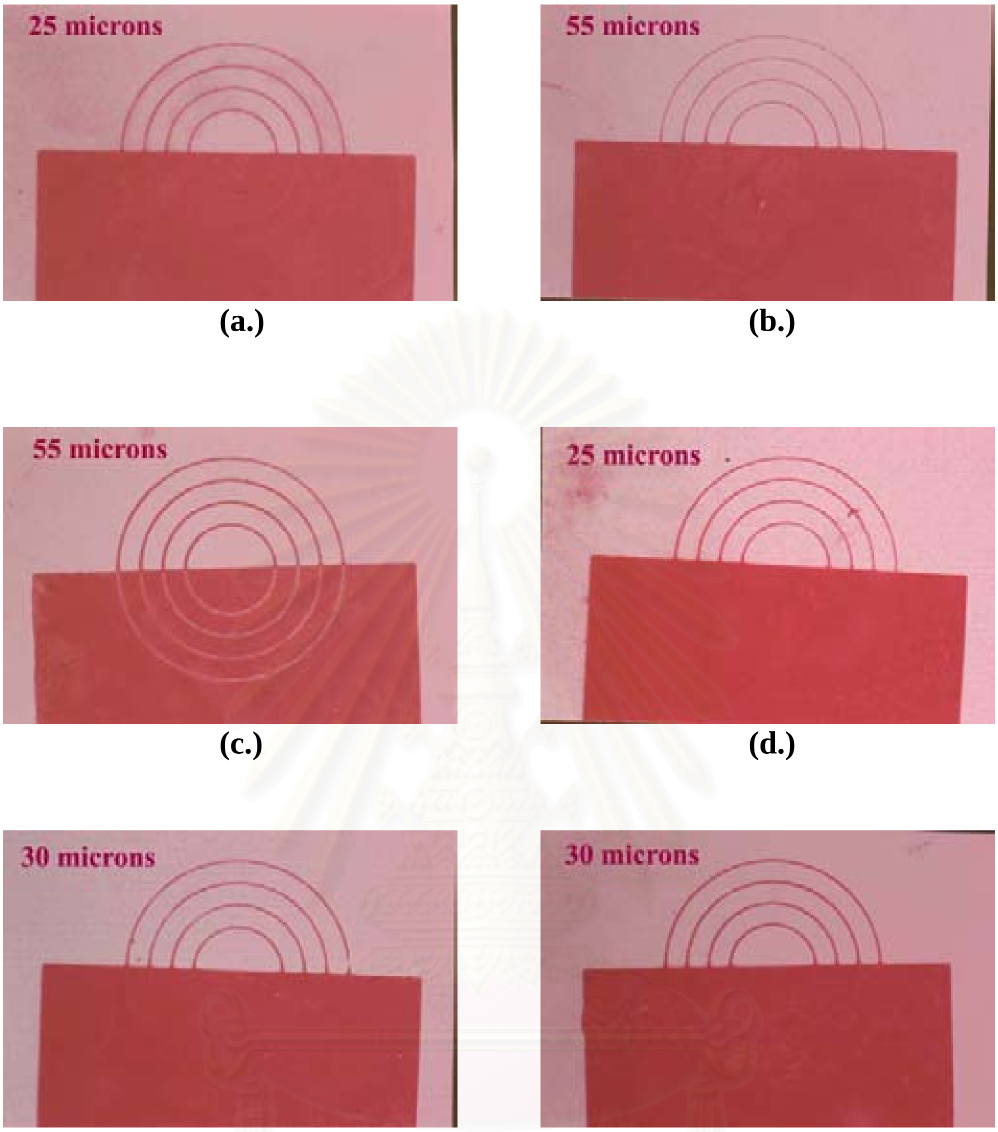
Runs	Exposure time (units)	Micro-line line width (μm)	
		Beginning point	Perfect point
T13	67	6	25
(M_w = 79,000	90	12	55
PDI = 2.2)	114	6	55
	134	8	25
	144	8	30
	154	6	30
T16-70	134	8	40
(M_w =128,000	154	8	25
PDI = 69,000)	184	8	40
	214	8	30
T16-80	134	55	55
(M_w =129,000	154	30	55
PDI = 2.2)	184	20	30

Figures 4.22a to 4.22d indicate that the resulting negative plate T13, at the exposure time of 114 units or 55 sec, has the complete positive and negative microlines at 55 μm, that is, the best exposure condition and resolution of the plate. However, the nearly complete positive and negative microline at 40 μm was resulted from the negative plate T16-70 at the exposure time of 134 units or 64 sec being considered also as a quite good exposure condition and resolution.



(a.) (b.) (c.) (d.) (e.)

Figure 4.22a The micro-line line width of the beginning point (left), perfect point (right), and optimum resolution from the resulting negative plate T05 at the exposure times of: (a.) 114 units, half positive microline at 20 μm, (b.) 124 units, half positive microline at 25 μm, (c.) 134 units, half positive microline 20 μm, (d.) 144 units, half positive microline 25 μm, and (e.) 184 units, half positive microline 25 μm.



(a.) (b.)

(c.) (d.)

(e.) (f.)

Figure 4.22b The micro-line line width of the beginning point (left), perfect point (right), and optimum resolution from the resulting negative plate T13 at the exposure times of: (a.) 67 units, halfpositive microline 25 μm, (b.) 90 units, half positive microline 55 μm, (c.) 114 units, complete microline (positive and negative) 55 μm, 134 units, half positive microline at 25 μm, (d.) 144 units, half positive microline at 30 μm, and (e.) 154 units, half positive microline at 30 μm.

(a.)

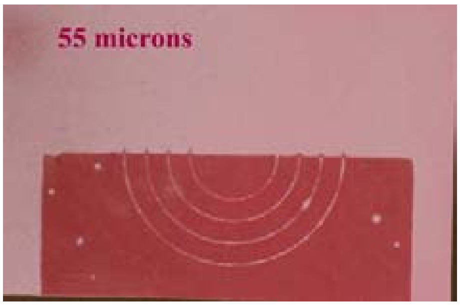
(b.)

(c.)

Figure 4.22c The micro-line line width of the beginning point (left), perfect point (right), and optimum resolution from the resulting negative plate T16-70 at the exposure times of: (a.) 134 units, almost complete positive microline at 40 μm.

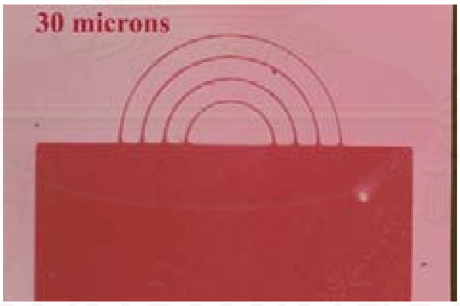
(b.) 184 units, half positive microline at 40 μm.

(c.) 214 units, half positive microline at 30 μm.



(a.)

(b.)



(c.)

Figure 4.22d The micro-line line width of the beginning point (left), perfect point (right), and optimum resolution from the resulting negative plate T16-80 at the exposure times of:

(a.) 134 units, half negative microline at 55 µm.

(b.) 154 units, half positive microline at 55 µm.

(c.) 184 units, half positive microline at 30 µm.

4.2.6 Determination of Hydrophilic/Hydrophobic Properties of the Resulting Plate

From the lithographic plate, a lithographic image is transferred from a flat surface. Certain areas on the surface are chemically treated to accept ink, and other areas are left untreated so that they will repel ink. When the surface is inked, the ink remains in the ink-receptive areas, but not in the untreated areas. When the material such as paper contacts the surface, the ink is transferred to the paper[2]. So the difference of hydrophilic/oleophilic property between image and non-image area is very important for printing quality.

The first step in obtaining good adhesion and print quality is to assure that image area can accept ink (oleophilic) and the non-image area can receive water (hydrophilic). As a result, the more interfacial area between the liquid and substrate, the greater the possibility of achieving sufficient bonding.

To investigate hydrophilic/hydrohobic properties of the resulting plate, the Contact Angle Meter (FACE Kyowa Interface Science Co., Ltd., Model CA-A) was used to measure the contact angles of oleic acid (representing the hydrophobicity of oil) on image areas, and water on non-image areas of the surface of the resulting plate. Two contact angle values on the left and right sides of the droplet were taken.

Table 4.16 The contact angle of water, oleic acid and fountain solution on the image and non-image area on the surface of the negative plate.

Plate		Liquid	Contact angle average(degrees) at the equilibrium point	
Runs	**Exposure time, units**		**Image area**	**Non-image area**
T05	114	Water	32	11
		Oleic acid	14	33
		FS[a]	25	6
	124	Water	41	10
		Oleic acid	12	30
		FS	38	5
	134	Water	42	11
		Oleic acid	13	34
		FS	42	5
	144	Water	42	14
		Oleic acid	15	33
		FS	52	5
	154	Water	50	10
		Oleic acid	14	31
		FS	50	4

Table 4.16 (continued)

Plate		Liquid	Contact angle average(degrees) at the equilibrium point	
Runs	**Exposure time, units**		**Image area**	**Non-image area**
T13	67	Water	50	10
		Oleic acid	14	29
		FS	42	8
	90	Water	49	9
		Oleic acid	16	30
		FS	36	5
	114	Water	46	14
		Oleic acid	13	32
		FS	40	8
	134	Water	46	10
		Oleic acid	15	33
		FS	44	4
	144	Water	57	11
		Oleic acid	13	32
		FS	49	3
	154	Water	50	10
		Oleic acid	13	32
		FS	49	8

Table 4.16 (continued)

Plate		Liquid	Contact angle average(degrees) at the equilibrium point	
Runs	**Exposure time, units**		**Image area**	**Non-image area**
T16-70	134	Water	54	18
		Oleic acid	15	26
		FS	42	5
	154	Water	62	15
		Oleic acid	19	36
		FS	33	6
	184	Water	43	14
		Oleic acid	18	40
		FS	34	8
	214	Water	57	8
		Oleic acid	14	22
		FS	43	8
T16-80	134	Water	51	14
		Oleic acid	14	32
		FS	31	3
	154	Water	57	16
		Oleic acid	18	41
		FS	55	3

Table 4.16 (continued)

Plate		Liquid	Contact angle average(degrees) at the equilibrium point	
Runs	**Exposure time, units**		**Image area**	**Non-image area**
	184	Water	52	11
		Oleic acid	15	42
		FS	48	6
T16-50	134	Water	56	13
		Oleic acid	17	32
		FS	70	8
	154	Water	50	16
		Oleic acid	13	41
		FS	36	5
T24	134	Water	54	13
		Oleic acid	15	36
		FS	36	7
	154	Water	51	14
		Oleic acid	16	43
		FS	42	4
	184	Water	58	12
		Oleic acid	13	42
		FS	55	4

[a] FS = Fountain Solution

Table 4.16 shows the average contact angles of water and oleic acid on the surface of the negative plate prepared from various copolymer binders at the specific exposure time. The resulting contact angle values indicate that image area is relatively oleophilic or hydrophobic because the oil contact angle values are smaller than the contact angle values of water on that surface. It means the surface accepts oleic acid (oil representing ink). On the other hand, the non-image area of the resulting plate is hydrophilic because the contact angle values of water is smaller than the contact angle value of oleic acid (oil). Basically, the small difference of the contact angles of water and oleic acid between image and non-image area can satisfy the requirement of lithographic plate. When the surface is inked, the ink remains in the ink-receptive areas, and some in the non-image areas. When the material such as paper contacts the plate surface, the ink is at the image area mostly transferred to the paper, while the non-image areas produce scumming. So the difference of hydrophilic/oleophilic property between image and non-image area is very important for printing quality.

The reasons for the small difference between the contact angles of water and oleic acid are explained. The contact angles of water and oleic acid are smaller than 90°. Since the polymeric binder is poly(methyl methacrylate-*co*-methacrylic acid), which is the base polymer for active ingredients to disperse in. The polymer binder including the ingredients was coated on the anodized aluminium plate. The nature of methacrylic acid moiety in the polymer binder is quite hydrophilic in which water can wet. For oleic acid containing an acid group, it still can wet the methacrylic acid moiety, regardless of its chain length. Therefore, both water and oleic acid can thus wet the exposed image areas similar to printing ink. In this work, oleic acid was used in the place of methylene iodide, the commonly used liquid, because it vaporized fast at room temperature.

For the non-image areas, the anodized aluminium surface has a composition of $Al_2CO_3 \cdot 6H_2O$ with a surface energy of about 360 mN m^{-1}. Therefore, the surface can accept both water (surface tension of 72.8 mN m^{-1}) and oleic acid (about 37.3 mN m^{-1}) because both fluids have the smaller surface tensions, and some similarly polar groups.

When the plain water had been applied first to the plate and the ink was followed. The print would be smudgy because the non-image areas could accept ink more or less depending on the ink property. It is therefore recommended that fountain solution should be used instead of water. Table 4.17 gives the general ingredients and their functions of fountain solution.

Table 4.17 General information of fountain solution.

Ingredient	Function
Ethylene glycol	Blanket lubricant
Phosphate salts	pH balance, buffering
Weak acid	pH control, promote desensitizing effect
Cobalt nitrate	Promote ink drying
Chromium salts	Not clear
Glycol ether	Cleaner, alcohol replacement
Surfactants	Cleaning, Surface tension reduction
Gum arabic	Desensitization
Nitrate salts	Cure scratches

Table 4.17 (continued)

Ingredient	Function
Miscellaneous salts	Anti-stripping
Silicones	Defoaming
Chelating agents	Neutralize water hardness
Antimicrobial	Prevent algae formation

According to Table 4.17, one can see that the active ingredients for desensitizing the non-image areas are gum arabic, phosphate salts, ethylene glycol. The non-image areas are desensitized to repel the oleophilic ink. After applying this fountain solution, the ink that followed could only emulsify in the fountain solution to avoid scumming in the non-image areas.

Scumming occurs when non-image areas of the plate accept and transfer ink such that the print does not remain completely clear in these areas. Obviously, scumming becomes a problem when ink transfer in the non-image areas becomes apparent to the naked eye or when it affects tonal rendition by increasing apparent density in halftone areas.

The physical characteristics, of the emulsified ink, can have a major impact on scumming. Problems may arise because the ink has too low a viscosity possibly caused by over-reduction or elevated temperature. Ink may then transfer over the top of the fountain film on the non-image areas. Excessive emulsification may also lead to a greater attraction between emulsified ink and fountain solution, leading to the same effect.

From Table 4.16, the higher contact angle of fountain solution on the image surface prevents the formation of a continuous film of damp. However, reticulated droplets of dampening solution do remain and could be expected to prevent ink transfer in the image areas that they cover. This is avoided with properly formulated litho inks since they are able to emulsify the tiny fountain droplets into the ink film to give a continuous image. This limited attraction between ink and water and its ability to take up water are fundamental to the success of the litho process.

There are number of factors at work which prevent the ink from forming a film across the top of the non-image fountain layer. Despite their plate differences in surface tension and chemical nature, there is a fundamental attraction between ink and water. A composite film of ink and fountain solution is formed together with partial emulsification of water in the ink. It is relative viscosities of the various components that determines how the film splits. Thus the much lower viscosity fountain solution will split in preference to the ink film, leaving a film of fountain solution on the non-image area and transfering some droplets of fountain solution onto the ink film which subsequently emulsify into the ink. Thus, according to this theory, the ink will not form a layer over the fountain solution. When applied to lithography, the distinction between image and non-image areas is sufficient to cause the following effects:

(a.) aqueous fountain solution spreads on the non-image area because of its low contact angle.

(b.) aqueous fountain solution in the image area is unable to form the continuous film because of its high contact angle, leaving th image free to accept ink.

However, the contact angle of aqueous fountain solution in the image area is smaller than 90°. Since the polymeric binder is poly(methyl methacrylate-*co*-methacrylic acid), which is the base polymer for active ingredients to disperse in. The nature of methacrylic acid moiety in the polymer binder is quite hydrophilic in which both water and aqueous fountain solution can wet the image area. The attraction of fountain solution in the non-image area is promoted by the use of the hydrophilic colloids, such as gum arabic, etc., activated with acid, which are present on the surface of the plate and incorporated into the fountain solution to maintain replenishment during the print run. Such colloids adhere to the non-image area surface and increase its hydrophilic nature such that displacement of the non-image fountain film by ink does not occur. Since the contact angles of water and fountain solution, which are smaller than 90° (on the image area), water can wet this area and function as a barrier between the ink and the non-image area. The printing experiment was thus performed [60].

4.2.7 Printing Experiment

The printing experiment was investigated as described in Section 3.7.4. The plate was first covered with the fountain solution (20-30 cm^3) for desensitizing the non-image areas and the ink was applied after.

The prints obtained have good seperation between the image and non-image areas. No ink was transferred in the non-image areas. The non-image areas were clean and paper white.

Eventhough the contact angle result indicates that both image and non-image areas can be wetted by both ink and water, but after using the fountain solution as the desensitizer, then the non-image area cannot be wetted by ink. That means the difference between image and non-image areas has occurred and the polymeric binder and UV coating formulation can be used to obtain the lithographic plate property. But the quality of printing depends on the ink quality. The images from the resulting negative printing plates are shown in the following Figure 4.23. These images are not of good printing quality because the ink has too high viscosity.

To this state, we can state that the copolymer of methyl methacrylate and methacrylic acid so produced can function well as a polymeric binder for lithographic negative plate that are developable by aqueous-base developer.

4.2.8 Adhesion Test

Pressure-sensitive tape (3M 610 brand or equivalent) was pressed onto the coating area on the surface of aluminium substrate. The pressure-sensitive tape was pulled straightly and peeled off to observe the coating marks on the tape according to ASTM D 3359-97. It was found that the adhesive tape test did not remove much of the coating from the surface. The results show that the photosensitive coating has a good adhesion to the aluminium substrate and the printing plates will be very long-life. The film forming property of this polymer is very strong that withstands adherence and withdrawal of high viscosity and tack of offset inks.

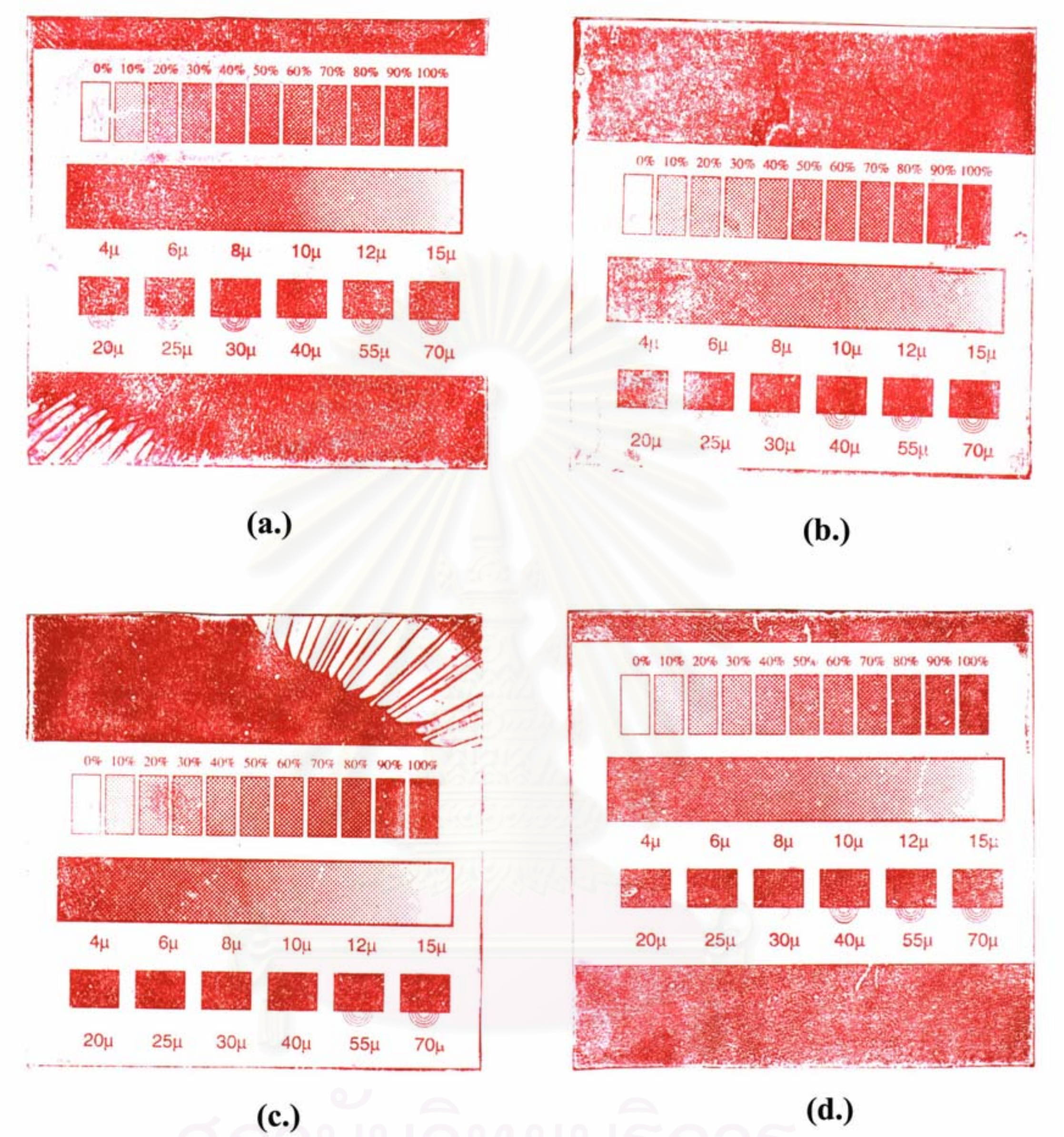


Fig 4.23 Printing qualities on paper from the synthesized binder/monomer system:(a) T05, 114 units; (b) T05, 124 units; (c)T16-80, 154 units; (d)T16-80, 184 units.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

The synthesis of the copolymer of methyl methacrylate and methacrylic acid was carried out by free radical polymerization for preparing the UV-sensitive aqueous base developable lithographic printing plate. In this research, several reaction parameters were investigated to find the appropriate condition for the copolymer binder to be used as a prepolymer of a UV-coating formula.

The appropriate condition for the preparation of poly(methyl methacrylate-*co*-methacrylic acid) prepolymer or binder could be concluded as follow:

- isopropyl alcohol concentration : 75% w/w
- comonomer concentration : 25% w/w
- monomer ratio MMA:MAA : 80:20
- initiator (BPO) concentration : 1% w/w
  (based on total comonomer concentration)
- reaction temperature : 70°C
- reaction time : 16 hours
- agitation rate : 295 rpm

The resulting copolymers were transparent and very rigid like a glass and had the following properties: the copolymer containing a ratio of MMA:MAA of 80:20 has the glass transition temperature (Tg) 163.4°C and average weight molecular weight of 1×10^6.

These copolymers were suitable for use as the binder of the UV coating on the anodized aluminium substrate (lithographic plate) because of their sensitivity to UV radiation, aqueous-base solubility and their good filmforming properties. Different ratios of these copolymers were mixed with the photosensitive material comprising the photosensitive monomers, TPGDA and TMPEOTA; the photoinitiators, Darocur 1173 and Darocur BP; and a pigment. The photosensitive coating was coated onto the anodized aluminium substrate by spin coating, which formed a smooth film, then overcoated by a PVA solution. An UGRA-like plate control wedge was assembled, and was exposed to UV radiation at many exposure times. The exposed plate was developed in an aqueous-base alkaline developer. The resulting plate was evaluated by percentage dot areas at 40, 50 and 60%, optimum resolution (microline), wettability by contact angles of water (on non-image area) and oleic acid (on image area) and adhesion test by 3M 610 standard tape.

The suitable pigment and developer for these UV coating formulations are anthraquinone and aqueous-base developer, respectively. The resulting plate is therefore a negative working plate.

Evaluation of the plate was made to prove that it had the properties of a surface printing plate and provided the appropriate lithographic plate properties. The plate provided a clean print, because of the difference of hydrophobic/hydrophilic property between the image and non-image areas. The plate gave a good adhesion evaluated by a standard tape test. The advantage of the negative working plate from the synthetic copolymers is that they have the aqueous-base soluble properties which are beneficial to our environment.

5.2 Suggestion for Future Work

Synthesis of poly(methyl methacrylate-co-methacrylic acid) for UV-sensitive aqueous-base developable lithographic plate would be further studied as follows:-

a.) Using other monomers in order to obtain new types of copolymer for preparing the UV-sensitive aqueous-base developable lithographic plate.

b.) Using other types of photosensitive coating formula for UV-coating which may produce better properties of printing plate.

c.) Using other kinds of the additive to attain a good quality printing plate.

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APPENDICES

APPENDIX A

Data of %dot area of the original film and the reproduction of the negative plate by various copolymer binders at the function of exposure time

Table A-1 Relationship of %dot area between the original film (UGRA plate control wedge) and the reproduction of the negative plate prepared by the copolymer binder (T05) that carried out for 5 hours reaction time and at MMA:MAA ratio of 70:30.

D_o[c]	**D_r**[a] **at any exposure time (units)**[b]				
	114	124	134	144	184
37.919	51.506	40.213	45.504	43.663	46.714
46.761	60.914	52.493	54.223	52.363	61.483
56.920	69.559	63.665	61.170	58.687	69.713

[a] D_r = %Dot area of the reproduction (the resulting plate)

[b] 1 unit = 0.48 sec

[c] D_o = %Dot area of the original film (UGRA plate control wedge)

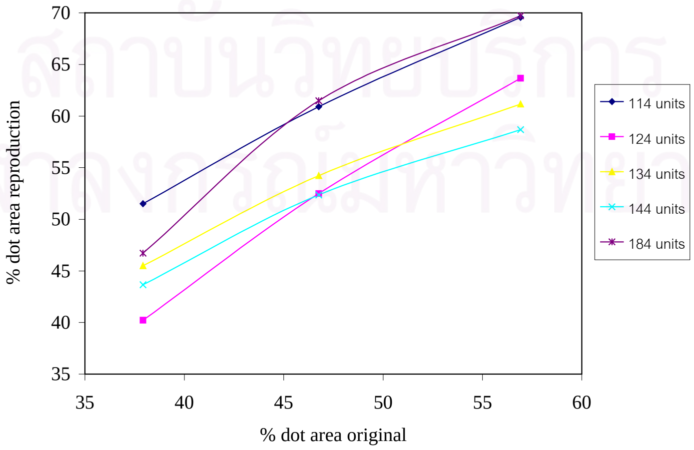

Figure A-1 Relationship between %dot area original film and reproduction of the negative plate prepared by copolymer binder T05 at any exposure time.

Table A-2 Relationship of %dot area between the original film (UGRA plate control wedge) and the reproduction of the negative plate prepared by the copolymer binder (T13) carried out for 13 hours reaction time and at MMA:MAA ratio of 70:30

D_o[c]	D_r[a] at any exposure time (units)[b]					
	67	90	114	134	144	154
37.919	43.313	39.174	40.067	41.333	39.837	42.105
46.761	53.427	50.332	52.538	55.115	51.315	57.551
56.920	62.351	59.297	62.258	63.217	61.753	65.513

[a] D_r = %Dot area of the reproduction (the resulting plate)

[b] 1 unit = 0.48 sec

[c] D_o = %Dot area of the original film (UGRA plate control wedge)

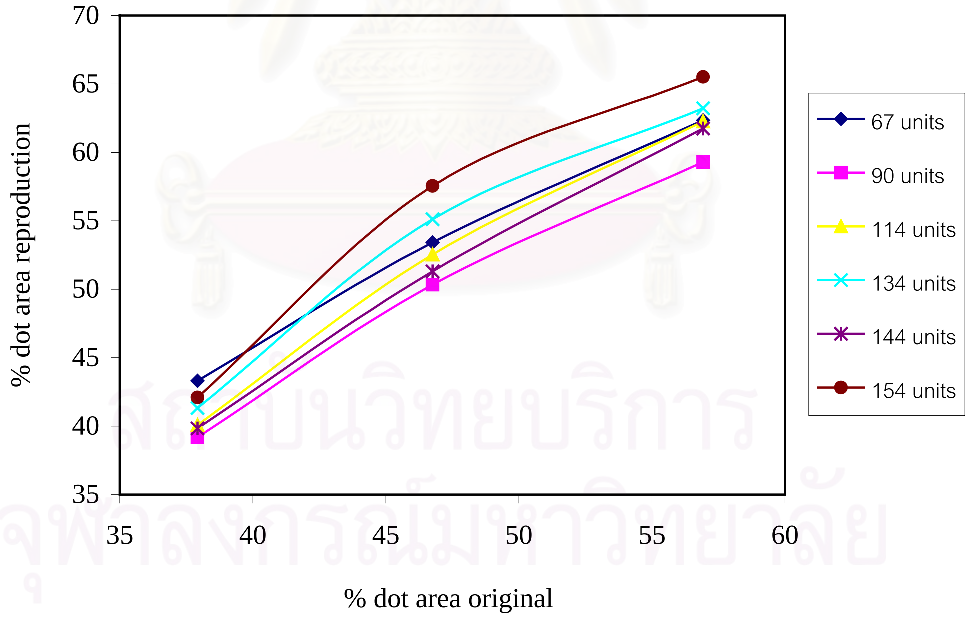

Figure A-2 Relationship between %dot area original film and reproduction of the negative plate prepared by copolymer binder T13 at any exposure time.

Table A-3 Relationship of %dot area between the original film(UGRA plate control wedge) and reproduction of the negative plate prepared by copolymer binder (T16-70) that carried out at 16 hours reaction time and MMA:MAA 70:30.

D_o[c]	**D_r[a] at any exposure time (units)[b]**			
	134	154	184	214
37.919	40.353	40.998	41.878	46.867
46.761	53.415	57.718	54.384	61.538
56.920	59.724	65.102	66.610	68.034

[a] D_r = %Dot area of the reproduction (the resulting plate)

[b] 1 unit = 0.48 sec

[c] D_o = %Dot area of the original film (UGRA plate control wedge)

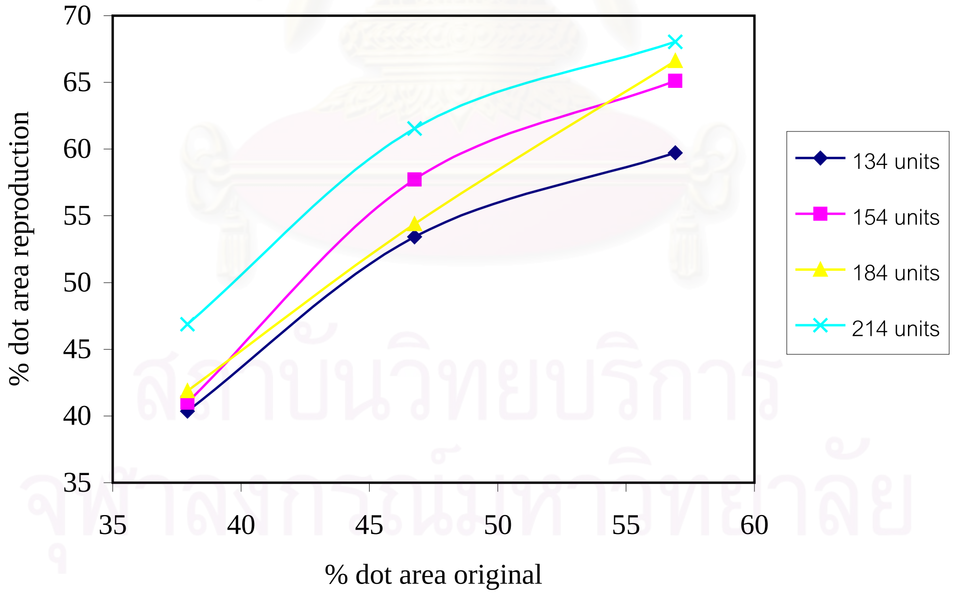

Figure A-3 Relationship between %dot area original film and reproduction of the negative plate prepared by copolymer binder T16-70 at any exposure time.

Table A-4 Relationship of %dot area between the original film(UGRA plate control wedge) and reproduction of the negative plate prepared by copolymer binder (T16-80) that carried out at 16 hours reaction time and MMA:MAA 80:20

	D_r[a] at any exposure time (units)[b]		
D_o[c]	134	154	184
37.919	31.363	38.580	43.722
46.761	40.547	49.510	55.265
56.920	55.757	59.837	66.784

[a] D_r = %Dot area of the reproduction (the resulting plate)

[b] 1 unit = 0.48 sec

[c] D_o = %Dot area of the original film (UGRA plate control wedge)

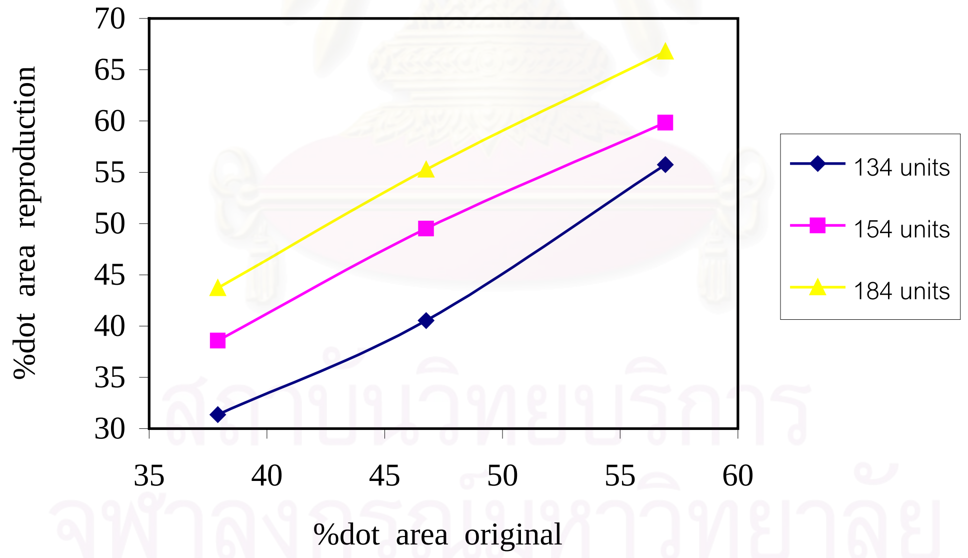

Figure A-4 Relationship between %dot area original film and reproduction of the negative plate prepared by copolymer binder T16-80 at any exposure time.

Table A-5 Relationship of %dot area between the original film(UGRA plate control wedge) and reproduction of the negative plate prepared by copolymer binder (T16-50) that carried out at 16 hours reaction time and MMA:MAA 50:50.

	D_r[a] at any exposure time (units)[b]	
D_o[c]	134	154
37.919	53.787	55.913
46.761	65.252	64.208
56.920	74.757	76.852

[a] D_r = %Dot area of the reproduction (the resulting plate)

[b] 1 unit = 0.48 sec

[c] D_o = %Dot area of the original film (UGRA plate control wedge)

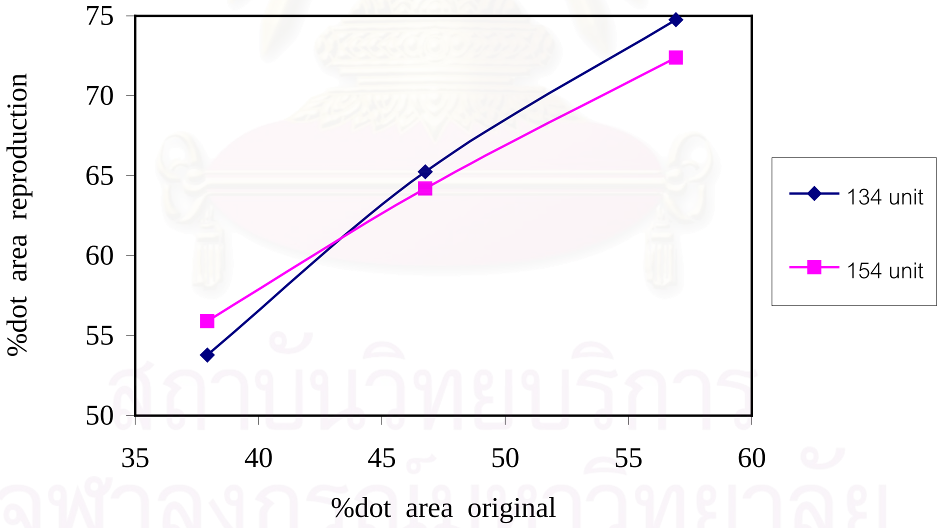

Figure A-5 Relationship between %dot area original film and reproduction of the negative plate prepared by copolymer binder T16-50 at any exposure time.

Table A-6 Relationship of %dot area between the original film (UGRA plate control wedge) and reproduction of the negative plate prepared by copolymer binder (T24) that carried out at 24 hours reaction time and MMA:MAA 70:30.

D_o[c]	D_r[a] at any exposure time (units)[b]		
	134	154	184
37.919	41.586	39.605	41.000
46.761	53.550	49.413	51.554
56.920	62.052	59.853	61.423

[a] D_r = %Dot area of the reproduction (the resulting plate)

[b] 1 unit = 0.48 sec

[c] D_o = %Dot area of the original film (UGRA plate control wedge)

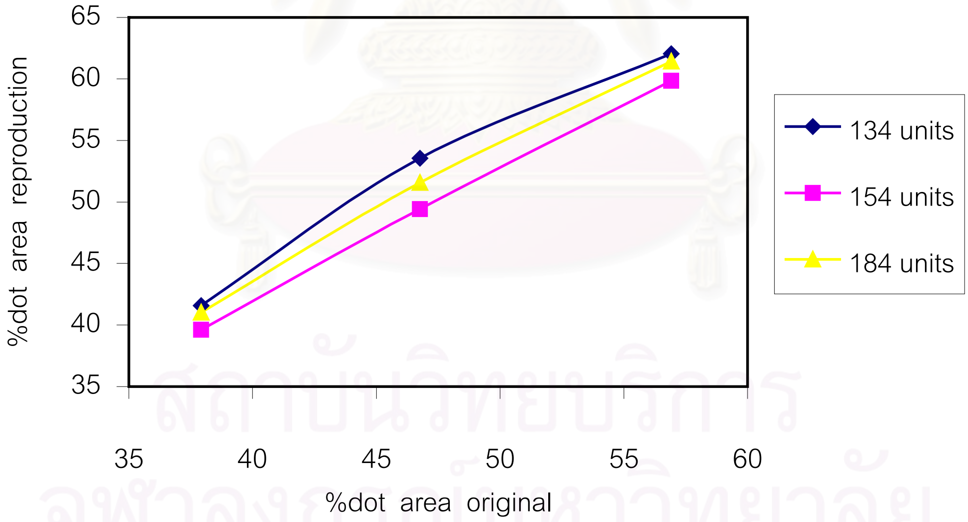

Figure A-6 Relationship between %dot area original film and reproduction of the negative plate prepared by copolymer binder T24 at any exposure time.

APPENDIX B

Data of contact angle of water and oleic acid at image and non-image areas on the surface of negative plate

Table B-1 The contact angle of water and oleic acid at image and non-image area on the surface of the resulting plate.

Plate		Solution	Contact angle average(degree) at equilibrium point	
Runs	Exposure time		Image area	Non-image area
T05	114 unit	Water	32.00	11.00
		Oleic acid	13.83	33.00
		FS[a]	25.00	5.83
	124 unit	Water	40.83	9.70
		Oleic acid	12.17	30.17
		FS	37.67	4.67
	134 unit	Water	41.83	10.67
		Oleic acid	13.17	33.50
		FS	41.67	5.17
	144 unit	Water	41.67	14.33
		Oleic acid	15.00	33.17
		FS	51.50	6.83

Table B-1 (continue)

Plate		Solution	Contact angle average(degree) at equilibrium point	
Runs	**Exposure time**		**Image area**	**Non-image area**
	154 unit	Water	50.00	10.17
		Oleic acid	13.67	30.83
		FS	50.33	6.83
T13	67 unit	Water	49.83	10.33
		Oleic acid	13.50	28.83
		FS	41.83	7.83
	90 unit	Water	48.83	9.00
		Oleic acid	16.17	29.67
		FS	35.50	5.00
	114 unit	Water	46.00	14.17
		Oleic acid	13.17	32.17
		FS	39.83	7.50
	134 unit	Water	45.83	10.33
		Oleic acid	15.00	33.17
		FS	43.67	4.33
	144 unit	Water	57.00	11.33
		Oleic acid	12.83	31.67
		FS	48.50	3.17

Table B-1 (continue)

Plate		Solution	Contact angle average(degree) at equilibrium point	
Runs	Exposure time		Image area	Non-image area
	154 unit	Water	49.67	9.67
		Oleic acid	12.83	31.83
		FS	57.17	7.67
T16-70	134 unit	Water	53.50	17.67
		Oleic acid	14.83	25.50
		FS	41.83	5.00
	154 unit	Water	62.17	15.00
		Oleic acid	18.83	36.17
		FS	33.33	5.67
	184 unit	Water	43.00	13.67
		Oleic acid	18.33	40.17
		FS	34.33	8.33
	214 unit	Water	57.17	7.667
		Oleic acid	14.17	22.33
		FS	32.00	7.50
T16-80	134 unit	Water	51.15	13.83
		Oleic acid	13.67	32.17
		FS	31.33	2.67

Table B-1 (continue)

Plate		Solution	Contact angle average(degree) at equilibrium point	
Runs	**Exposure time**		**Image area**	**Non-image area**
	154 unit	Water	56.50	15.50
		Oleic acid	18.00	41.17
		FS	55.83	3.17
	184 unit	Water	52.33	10.83
		Oleic acid	14.83	42.00
		FS	48.17	6.33
T16-50	134 unit	Water	56.33	12.50
		Oleic acid	17.00	32.17
		FS	69.83	8.00
	154 unit	Water	50.00	15.50
		Oleic acid	12.67	41.17
		FS	36.00	5.00
T24	134 unit	Water	54.33	12.83
		Oleic acid	14.50	36.00
		FS	35.67	7.17
	154 unit	Water	51.00	14.30
		Oleic acid	16.33	42.50
		FS	41.83	3.50
	184 unit	Water	57.83	11.67
		Oleic acid	12.83	42.33
		FS	57.17	3.83

[a] FS = Fountain Solution

APPENDIX C

The example of negative film control wedge and resulting negative printing plate

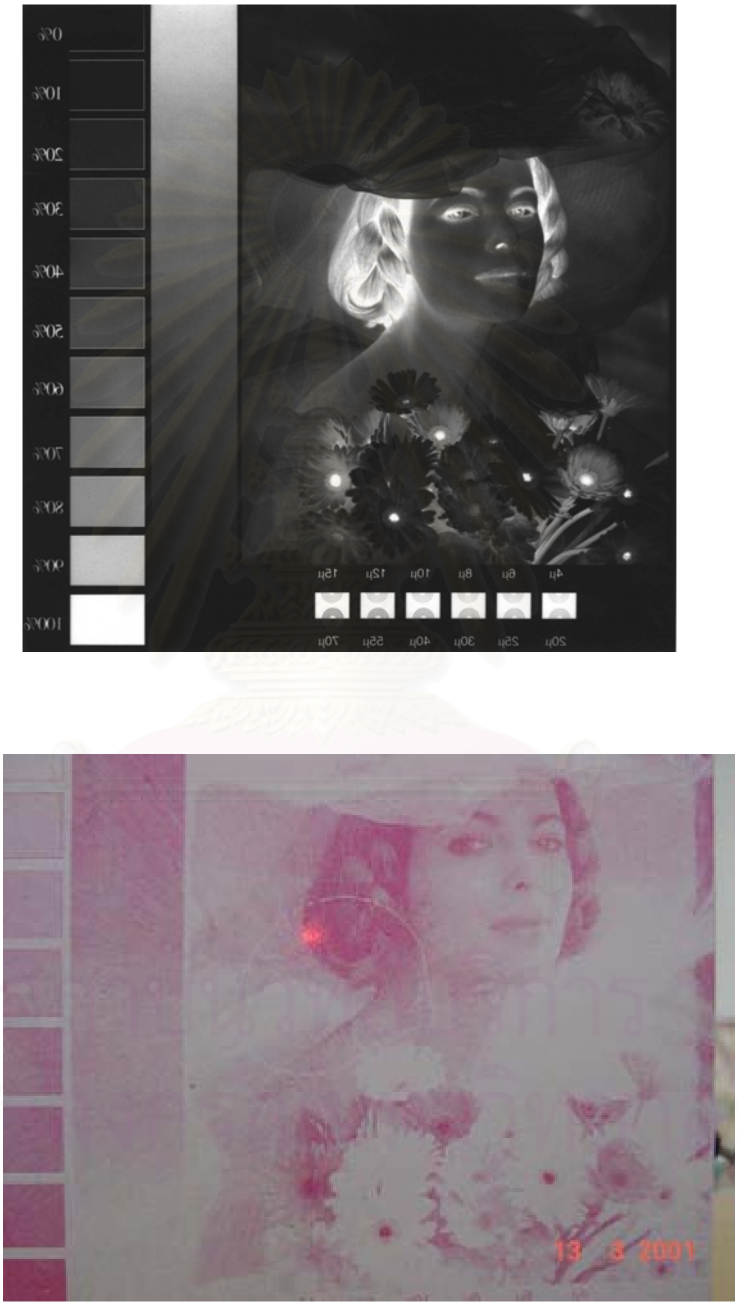

Figure C-1 (a.) Top center, negative film control wedge, UGRA-like plate.

(b.) Bottom center, the resulting negative plate from negative film (a.).

APPENDIX D

The Apparatus for UV coating irradiation

(a.)

Figure D-1 (a.) The UV exposure: TA SHIANG machine Co., Ltd., Model TS-VPF 32 SP-2, made in Taiwan.

(b.) **(c.)**

Figure D-1 (continued) (b.) Spin Coater : ABLE Co., Ltd., made in Japan.

(c.) Contact angle meter: FACE Kyowa Interface Science Co., Ltd., Model CA-A, made in Japan.

VITA

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