CHAPTER 4

RESULTS OF LASER MARKINGS ON FILM SUBSTRATE

Bearing in mind that the objective of film marking is to etch characters that can be projected on a theatre's screen, this project centres on investigating the optimum parameters that removes just the emulsion with clearly defined and straight edges but without altering the optical transmission of the substrate. The marking characteristics are investigated by studying the light transmission through the film.

This chapter is divided into three sections. The first section presents the digitised results of laser film markings showing the progression of the mark formation. The second section presents the qualitative analysis of the film markings. Here, the general characteristics of the laser-irradiated site are presented followed by characteristics specific to the CVL and Argon Ion laser markings. A comparison of the effects of different substrates is made.

The third section presents the quantitative analysis of the film markings using the techniques employed in the first section. The progression of the laser mark formation as a function of laser energy is measured and plotted in graphs. The effect of the Gaussian beam profile of the Argon Ion laser on the markings is also investigated.

4.1 FILM MARKING RESULTS.

Film marking is performed using the set-up as described in Section 3.3. A length of specially selected film with black and uniform background is mounted on the film advance unit. The motion picture film is divided into sequence of repeated frames. Each frame measures about 19 mm in height and 35 mm in width.

On each frame, a series of 30 lines is etched. The lines are divided into 2 columns of 15 lines each. Each line measures about 8 mm in length. Using a constant laser power, the first line is scanned from left to right at a constant velocity. The second line is etched on the same row but with a spacing of 1.5 mm between the columns. The velocity of the second line scanned is set to be slower than the first but at a fixed increment of time interval. The third line is then scanned below the first line with a spacing of 1.5 mm from the first row. The process is repeated for the rest of the lines until all the 30 lines are etched in 1 frame with the last line being the slowest. An identification mark using alphanumeric character indicating the laser power and scanner speed used is etched at the top of the film to aid retrieval for analysis later.

The Film Advance Unit is used to advance the film by two frames. The laser power is incremented and the etching process is repeated on a new frame. For Argon Ion laser, the laser power used is between 1 to 6 watts with 1-watt increment for each frame. For CVL, the laser power is varied according to the table below.

Frequency (kHz)	Average Power (W)	Irradiance (MW/cm^2)	Fluence (J/cm^2)
5	1.0	170	5.09
5	1.9	323	9.68
8	0.9	95	2.86
8	1.6	170	5.09
14	0.6	36	1.09

Table 4.1. CVL power used for etching.

Two sets of results using Triacetate and Polyester base film material are collected for each of the laser set-ups. A digitised image of the whole frame is shown in Figure 4.1. The magnified image of each line within the frame is digitised using the set-up described in Section 3.5.1.

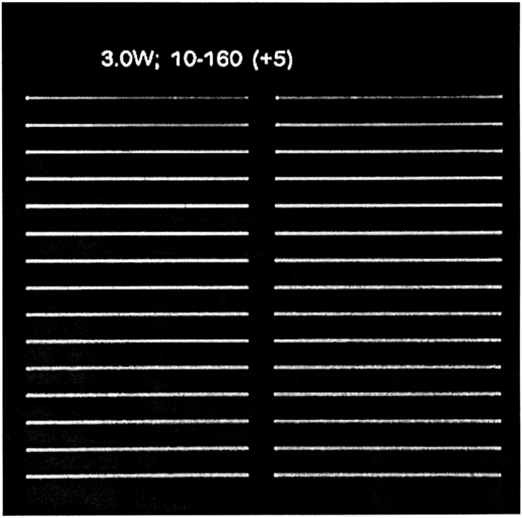


Figure 4.1. Digitised image of one frame showing identification marks and 30 lines.

4.1.1 CVL markings on Polyester film.

Figure 4.2 shows the CVL markings on Polyester film using 1.0 W. As etching at other power levels yields the same results, only 1 set of data is shown.

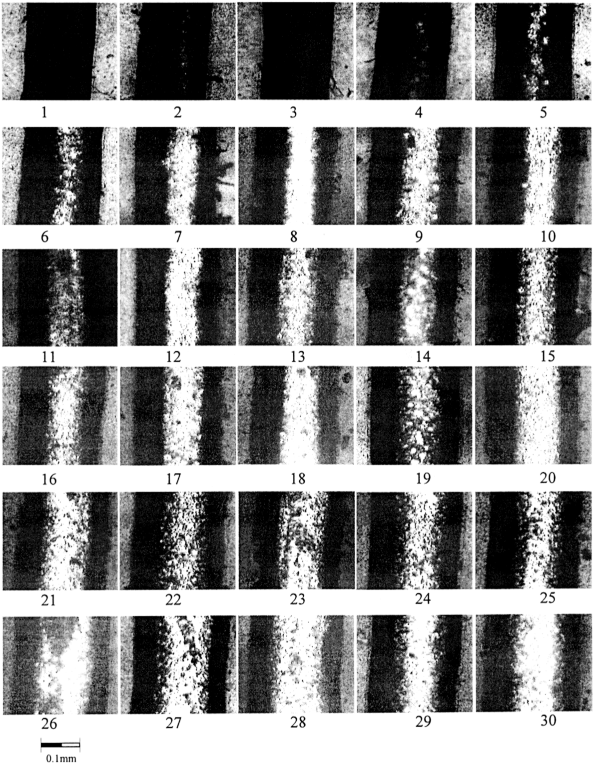


Figure 4.2: 1.0 W CVL markings on Polyester film.

4.1.2 Argon Ion laser markings on Polyester film.

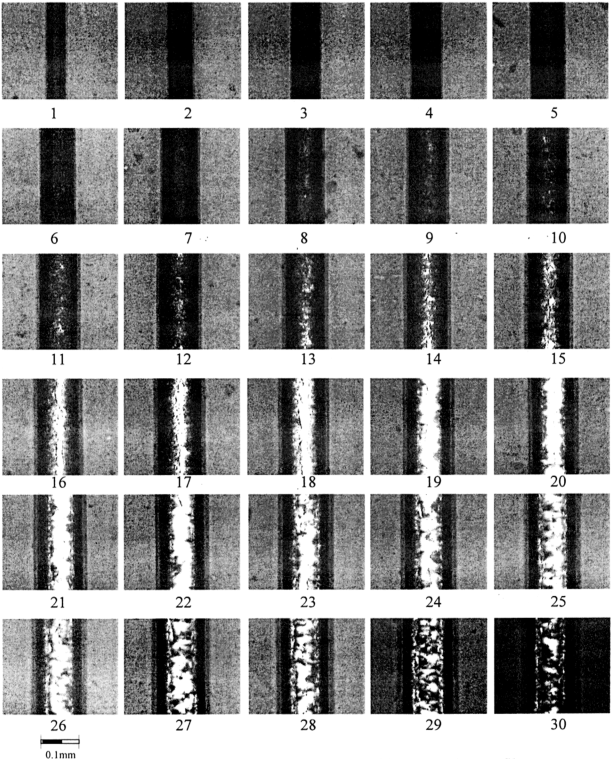


Figure 4.3: 1.5 W Argon Ion laser markings on Polyester film.

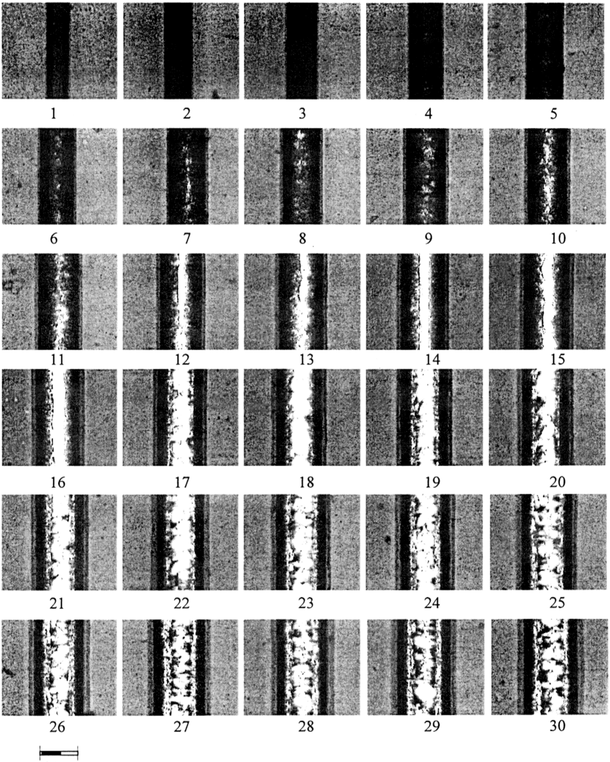
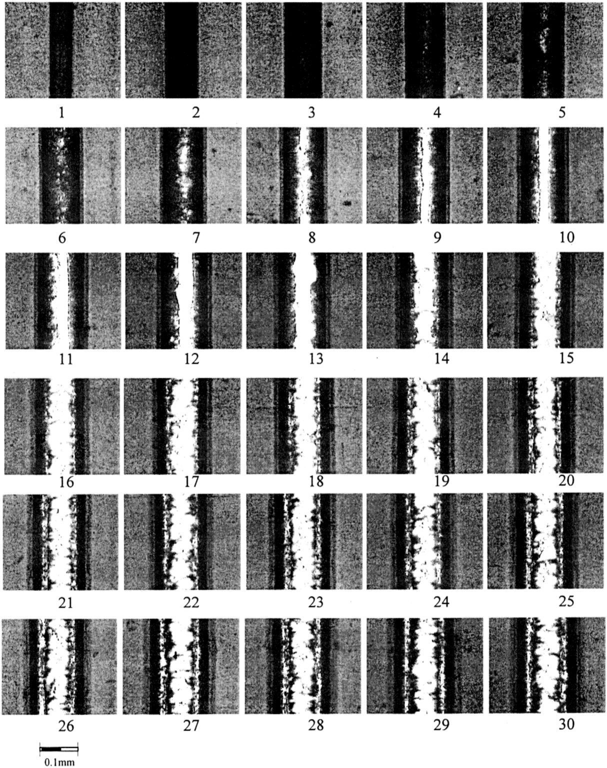


Figure 4.4: 2.0 W Argon Ion laser markings on Polyester film.



1 2 3 4 5

6 7 8 9 10

11 12 13 14 15

16 17 18 19 20

21 22 23 24 25

26 27 28 29 30

Figure 4.5: 3.0 W Argon Ion laser markings on Polyester film.

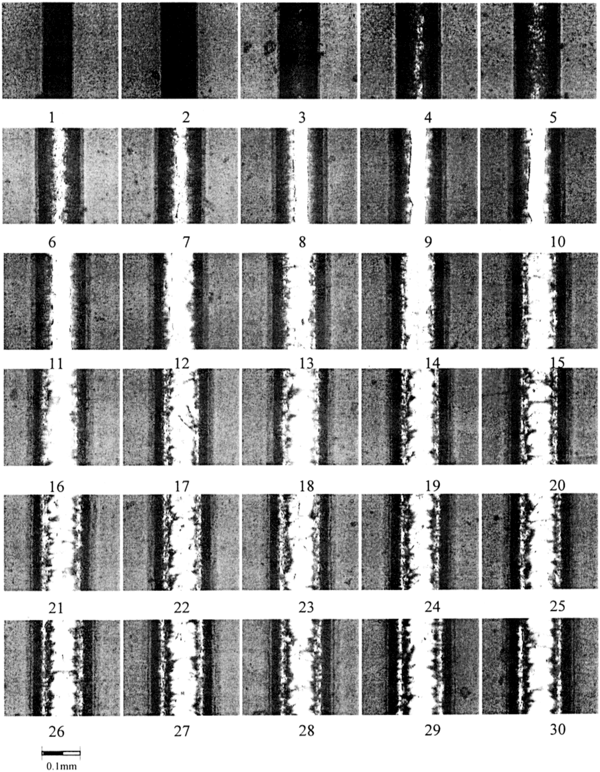


Figure 4.6: 4.0 W Argon Ion laser markings on Polyester film.

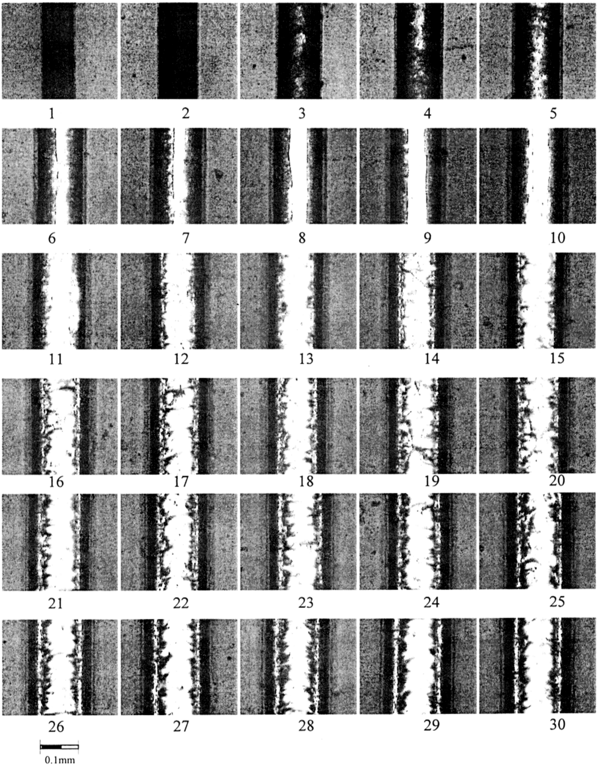


Figure 4.7: 5.0 W Argon Ion laser markings on Polyester film.

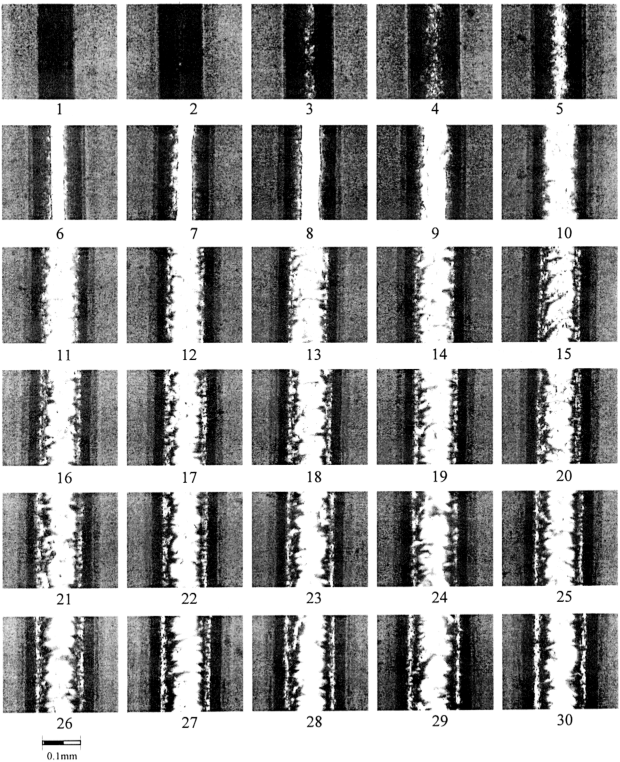


Figure 4.8: 6.0 W Argon Ion laser markings on Polyester film.

4.1.3 Argon Ion laser markings on Triacetate film.

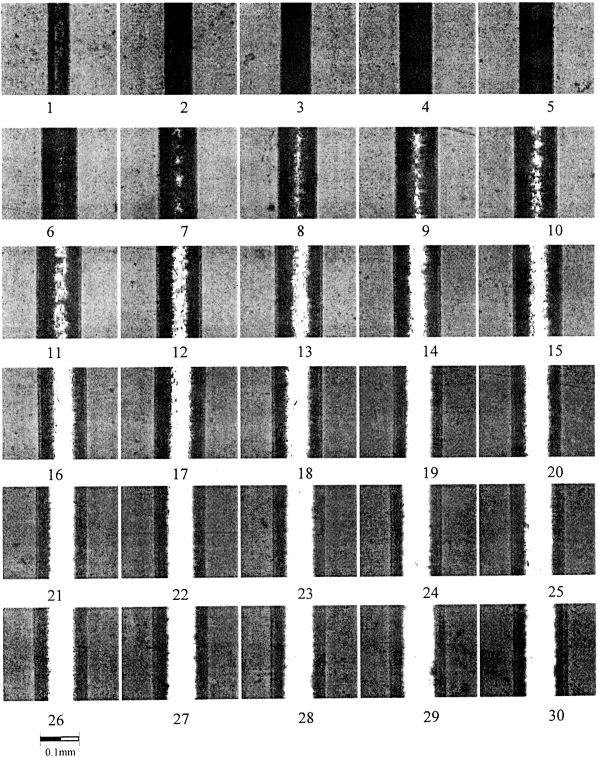


Figure 4.9: 1.5 W Argon Ion laser markings on Triacetate film.

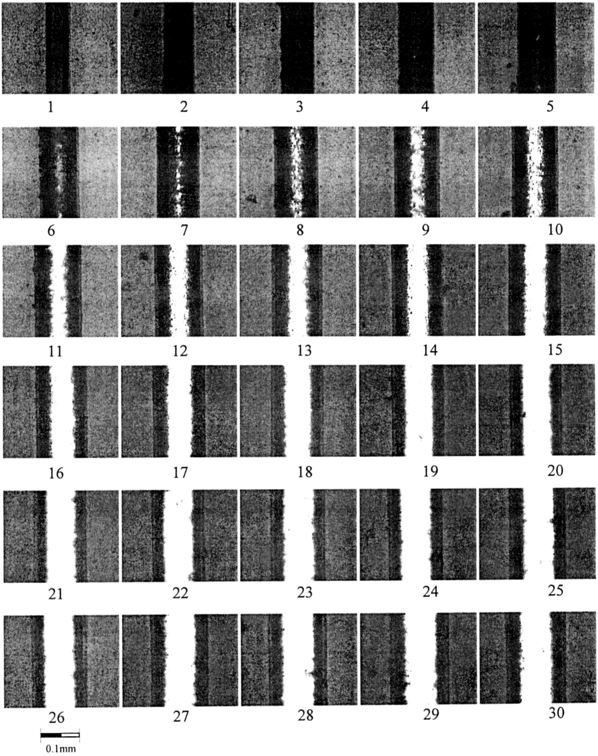


Figure 4.10: 2.0 W Argon Ion laser markings on Triacetate film.

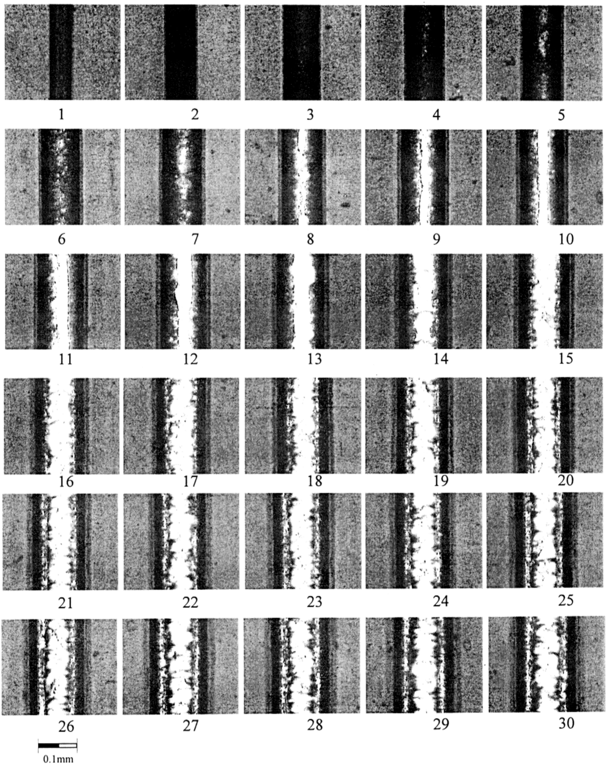


Figure 4.11: 3.0 W Argon Ion laser markings on Triacetate film.

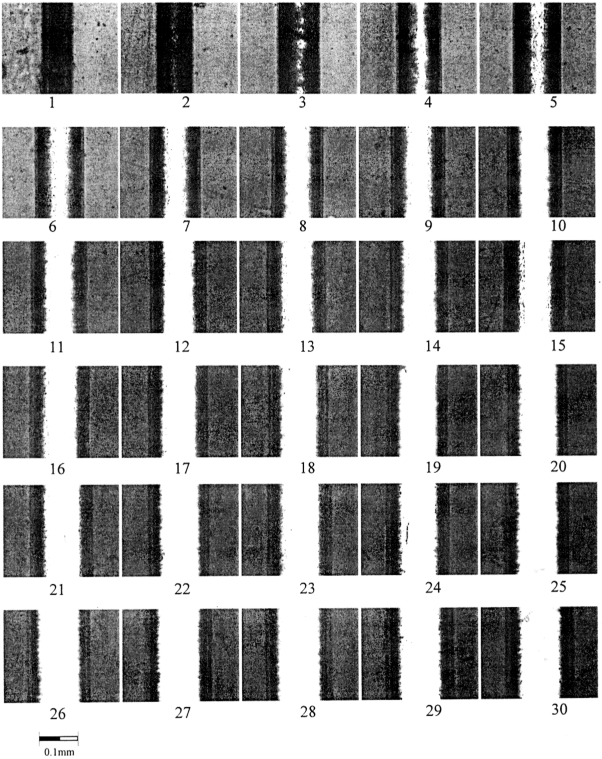


Figure 4.12: 4.0 W Argon Ion laser markings on Triacetate film.

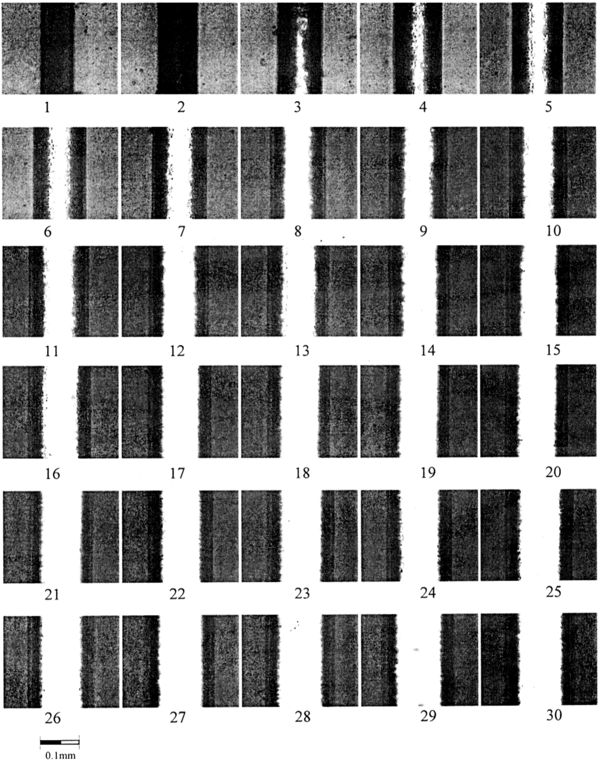


Figure 4.13: 5.0 W Argon Ion laser markings on Triacetate film.

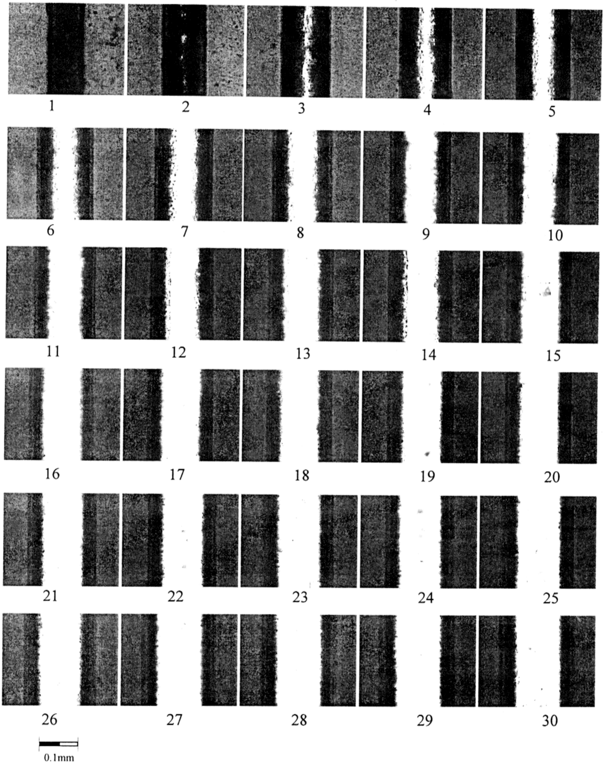


Figure 4.14: 6.0 W Argon Ion laser markings on Triacetate film.

4.2 QUALITATIVE ANALYSIS OF LASER MARKING QUALITY

4.2.1 Characteristic zones of laser-irradiated site

Figure 4.2 - 4.14 shows the progression of mark formation using different lasers and substrates. The first line was made with a fast scanning rate followed progressively by slower scanning rate. Initially the mark is formed with a small but consistent darkened area or heat affected zone (HAZ). At slower scanning speed, the HAZ grows in width and a lighter area start to form in the centre of the line. The lighter area, where the emulsion has vaporised, is shallow and irregular in width. As the width of the area increases, the colour of the light transmitting through the film changes from black (emulsion with thermal damage), green (first emulsion layer removed), yellow (second emulsion layer removed) and white (all emulsion layers removed).

The Clear Area, where emulsion is removed, starts forming irregular patches growing in size until an irregular line of Clear Area forms. The Clear Area becomes progressively regular in width until it forms uniformly clear line. Further increase in laser irradiation results in the Clear Area's line width becoming irregular again with the film substrate becoming increasingly distorted.

Post-exposure examination of the laser-irradiated area reveals 4 characteristic zones of thermal damage as shown in Figure 4.15.

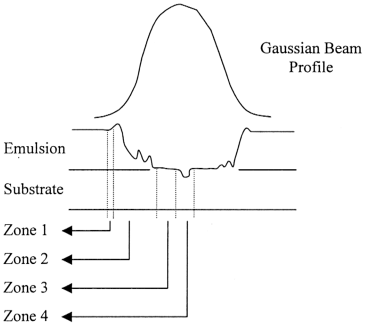


Figure 4.15: Characteristic zones of laser markings on film.

Zone 1 (Heat Affected Zone)

This is a very small heat affected zone about 8 micron in width. This zone shows slight distortion and change in colour but otherwise similar to the unirradiated area. Heat conducted from the vaporisation zone and possibly little absorption from the tail end of the Gaussian beam may cause the emulsion's temperature to rise close to its decomposition temperature. This width of this zone is small for lower power or slower scanning time and increasing in width for higher incident laser energy density.

Zone 2 (Partial Emulsion Vaporisation Zone)

This is the interface between the vaporised area and the unirradiated emulsion area. It is usually a steep slope black in appearance due to the emulsion's residue that underwent thermal decomposition. The slope also shows up as green and then yellow colour as the depth of the slope increases. The change in transmission colour is due to the number of emulsion's primary colour layers remaining.

At lower laser irradiation energy density, bubble-like formation is often seen at the bottom of the slope. The bubbles form because the emulsion's absorption in this area is sufficient to raise the temperature up to the vaporisation temperature where some emulsion vaporises. The remaining emulsion subsequently cools down after termination of laser irradiation. Sometimes, the bubbles appear more transparent due to decomposition. The width of this zone is very sensitive to the laser power density and scanning speed. At low laser energy density, this zone completely covers zone 3 and 4 areas. For an ideal etching, the width of this zone is approximately 10 microns.

Zone 3 (Clear Zone)

This is the area where the emulsion is completely removed by laser irradiation leaving the optically clear substrate layer. Ideally, the substrate layer should not be thermally affected. But at higher incident laser energy density, the substrate may be slightly deformed at temperatures exceeding the glass transition temperature and the thermal forces deform the substrate material in its rubbery state. At higher temperature, the substrate may even melt (for Polyester) and subsequently resolidify. However, the substrate is still optically transparent. The width of this layer determines the etching quality.

Zone 4 (Damaged Substrate Zone)

Usually starts from the centre of the laser irradiated area, this is the zone where substrate thermal damage occurs. Here, the substrate appears darkened with transparent micro-bubbles. This is caused by over-exposure to the laser irradiation where the substrate itself absorbs enough to thermally decompose. Longer exposure to the laser irradiation will cause vaporisation and substrate material removal from this area.

4.2.2 Characteristics of CVL Markings

Observation of CVL etching indicates that the etching process generates high velocity plumes with accompanying high-frequency sizzling sound. Close-up inspection of the surrounding irradiation site reveals the deposition of large amount of debris.

Zone 1 and Zone 2 area often shows distorted and structures of varying width. At lower power, zone 2 often extends into zone 3 area. The desired Zone 3 area appears yellowish possibly due to thermal damage to the substrate layer. More bubble-like formation is observed here. (Possibly, the residual emulsion has fused with the substrate due to high temperature). The distorted and wavy lines may be contributed by the following factors. Because multiple overlapping pulses are required to form the Clear Area, the width of the line is dependent on the pulse to pulse power stability of the laser, provided that the scanning velocity and pulse frequency is stable. CVL's pulse energy have been known to vary between shots to shots. Furthermore, there are reports of variation in the temporal energy distribution during the evolution of a single CVL pulse. This may be the cause of some reported CVL drilling process where the hole formation is described as starting with an initial irregular crater, deepens regularly with slight conicity and smooth walls, and finally ends with a constant shape [10].

Observations of the irradiated site, together with the laser fluence used (up to 10 J/cm^2), suggest that the primary etching mechanism is multi-pulse photothermal ablation.

Normally, the CVL pulse duration of 30 ns is too short for any significant radial heat conduction to occur, which is typically in the range of milliseconds. Because of this, temperature could jump to thousands of Kelvins at the ablation site. However, considering the emulsion layer is only about 8 microns, the extremely high temperature gradient in the emulsion layer can diffuse to a very thin substrate's surface layer. Contribution from the thermal process, coupled with absorption of the subsequent laser pulses by the substrate, may cause irreversible substrate thermal damage (yellowing). The yellowing effect has been reported by Bahners et. al. [11] in excimer laser ablation of poly(ethyleneterephthalate) or Polyester. It is argued that the ablation product (interacting with air) consists of ionised, carbon-rich material that finally condenses, forming higher aggregates. It has also been shown that the formation of the colouring layers can be avoided by applying a suitable impregnation medium prior to or during laser treatment. At higher fluences, the yellowing effect may further increase the absorption of subsequent laser pulses significantly, causing the vaporisation of substrate material (Zone 4) commonly observed in CVL etching. The fact that vaporisation starts in the centre of the line can be attributed to the beam profile of the CVL. As described in Section 3.2.1, the unstable resonator produces a beam with progressively smaller but higher intensity concentric rings. The extremely high intensity at the centre of the beam may ablate even transparent material [10], as in the case of 1 to 5 watts CVL drilling of glasses and crystals [13]. Usually, zone 4 starts to form even before zone 2's bubble-like formation fully clears. It appears as though CVL's pulses do not distinguish between emulsion and substrate material (non-selective etching).

4.2.3 Characteristics of Argon Ion Markings.

Argon Ion laser etchings generally exhibit very consistent line widths in all the zones previously described. Zone 1's width is usually consistent. Zone 2's width often varies at lower laser energy density but becomes more consistent as laser energy density increases. There is little or no residue on the film surface as compared to CVL etching.

At c.w. power of a few watts, the laser irradiation can be considered as a very high-energy heat source localised within the focused region. Emulsions having absorbed the sufficient laser irradiation are thermally decomposed into gas, which expands away from the film surface (vaporised). The substrate, however, transmits most of the irradiation and is generally not affected. The mechanism is consistent with non-ablative photothermal decomposition.

4.2.4 Comparison between Polyester and Triacetate Substrate Base

Etching quality of Triacetate substrates are generally better when compared to that of Polyester. Triacetate film usually has cleaner and more consistent Clear Area. This is because it is possible to etch Triacetate film at higher irradiation energy densities than Polyester film before substrate damage appears. Longer scanning time allows more complete emulsion removal. As reviewed in Section 2.5, Triacetate have higher glass transition temperature than Polyester and therefore is able to tolerate higher temperature. Polyester film on the other hand is quite sensitive to scanning rate and tends to deform easily before all emulsion material has been sufficiently removed leaving charred residue along the edges of the line.

4.2.5 Observations using SEM

Figure 4.16 (a) to 4.16 (e) shows the formation of the laser-etched lines at different stages viewed under the Scanning Electron Microscope. Figure 4.16 (a) shows the line formed using low irradiation energy density. The emulsion is thermally decomposed by the laser beam leaving charred residues. When viewed under conventional light transmission microscope, the line appears dark due to light scattering by the residues. Figure 4.16 (b) shows the line formed at higher irradiance. The emulsion in the centre of the line is vaporised by the laser beam leaving the substrate undamaged. The emulsion at the edge of the line is thermally decomposed but did not absorb sufficient energy to vaporise.

At optimum power and scanning speed, the emulsion is cleanly vaporised leaving the substrate almost undamaged as shown in Figure 4.16 (c). There is still some charred residues left at the edges of the line but their widths are relatively small when compared to the clear area in the centre. At even higher irradiation energy density, the residues at the edges of the line are reduced, but the substrate at the centre of the line starts to vaporise. Figure 4.16 (d) shows the pocket of holes left behind when the substrate is vaporised. The fact that the holes occur in the centre of the line points to the higher energy density in the centre of the Gaussian beam. It is also possible that the argon ion laser have transient energy surges due to localised transient hot-spot formation in the discharge tube. These holes are not detected through transmission microscope earlier. Perhaps the high light intensity transmitted through the substrate helps to obscure their presence.

Figure 4.16 (e) shows the substrate damage when too high irradiation energy density is used. Note that there are still some emulsion residues left at the edge of the line. The substrate residues have a different texture and appear quite transparent when viewed through the transmission microscope.

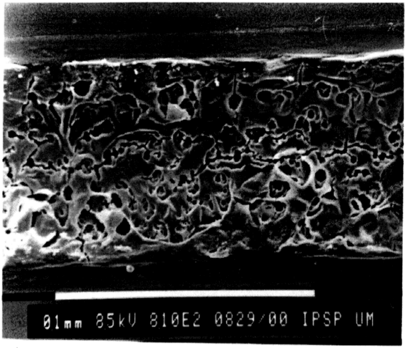


Figure 4.16 (a): HAZ formed by thermally decomposed emulsion.

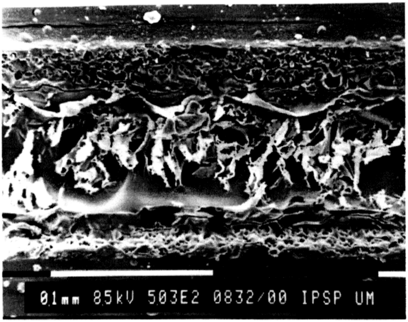


Figure 4.16 (b): Clear area begins to form.

Figure 4.16: Scanning Electron Micrographs of Argon Ion Laser etching on Polyester film.

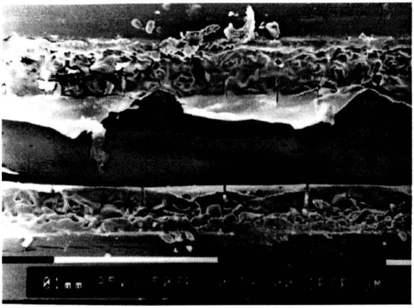


Figure 4.16 (c): Optimum marking with large clear area.

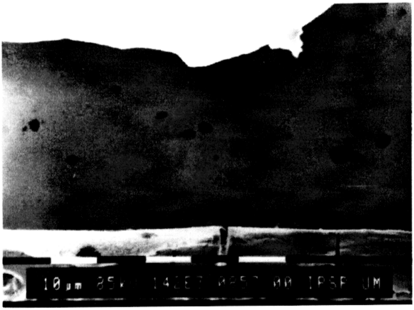


Figure 4.16 (d): Holes formed by vaporised substrate at the centre of the line.

Figure 4.16: Scanning Electron Micrographs of Argon Ion Laser etching on Polyester film.

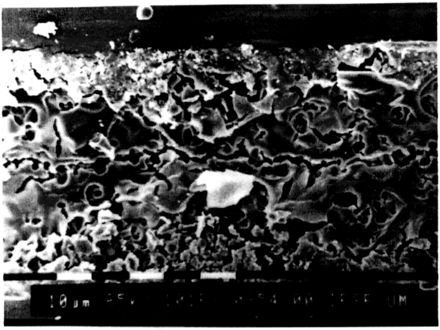


Figure 4.16 (e): Substrate damage.

Figure 4.16: Scanning Electron Micrographs of Argon Ion Laser etching on Polyester film.

4.3 QUANTITATIVE ANALYSIS OF THE LASER MARKINGS

Marking results of Copper Vapour Laser is not analysed here because almost all of the markings are inconsistent and varies in width. Such marking quality is not acceptable for film marking purposes. Only Argon Ion lasers, which produce good consistent markings, are quantitatively analysed.

Using the Digital Signal Processing set-up described in Section 4.1, the widths of the laser-marked lines are measured. For analysis purpose, two parameters are measured. The parameters are width of Clear Area and Heat Affected Zone (HAZ). The definition of both the parameters is defined in Section 4.1. The width of Clear Area is usually not consistent especially at lower powers or high scanning speed. Therefore, the maximum and minimum Clear Area widths are also measured. The width of HAZ is quite consistent and consequently only 1 measurement is taken for every line.

4.3.1 Effects of Laser Power and Irradiation Time on Marking Width

Figure 4.17 and 4.18 show the widths of the Clear Area and HAZ as a function of laser irradiation time. The laser irradiation time is the duration the laser's focused spot takes to traverse a distance equal to its spot diameter on the film surface. The error bar shows the maximum and minimum width of the Clear Area. For easier comparison of the effects of different irradiation power, Figure 4.19 to 4.22 shows the width of Clear Area and HAZ as a function of laser irradiation time using various irradiation power.

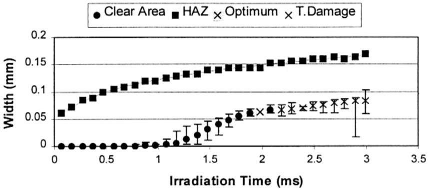


Figure 4.17 (a): Using 1.5 W Argon Ion Laser

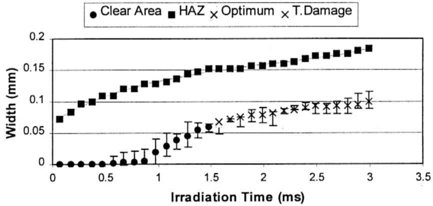


Figure 4.17 (b): Using 2.0 W Argon Ion Laser

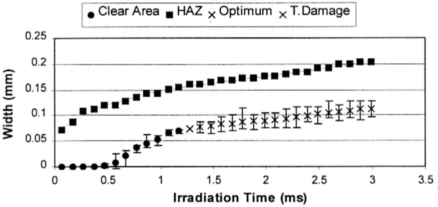


Figure 4.17 (c): Using 3.0 W Argon Ion Laser

Figure 4.17: Width of Clear Area and HAZ as a function of irradiation time for Polyester film.

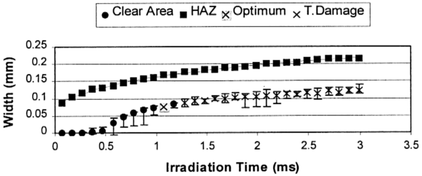


Figure 4.17 (d): Using 4.0 W Argon Ion Laser

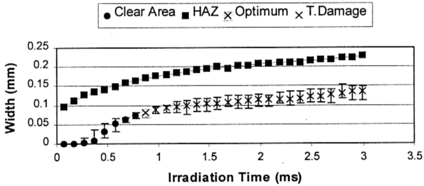


Figure 4.17 (e): Using 5.0 W Argon Ion Laser

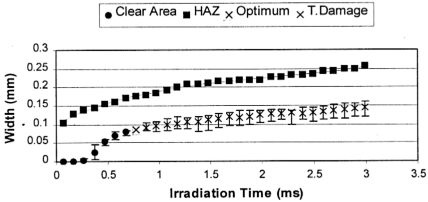


Figure 4.17 (f): Using 6.0 W Argon Ion Laser

Figure 4.17: Width of Clear Area and HAZ as a function of irradiation time for Polyester film.

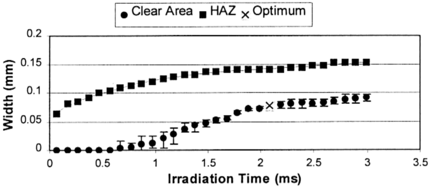


Figure 4.17 (a): Using 1.5 W Argon Ion Laser

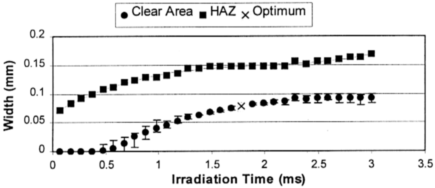


Figure 4.17 (b): Using 2.0 W Argon Ion Laser

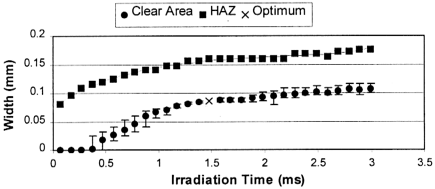


Figure 4.17 (c): Using 3.0 W Argon Ion Laser

Figure 4.18: Width of Clear Area and HAZ as a function of irradiation time for Triacetate film.

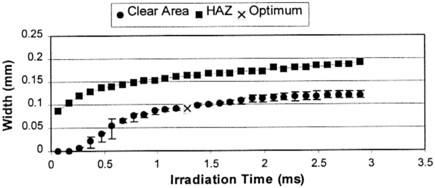


Figure 4.17 (d): Using 4.0 W Argon Ion Laser

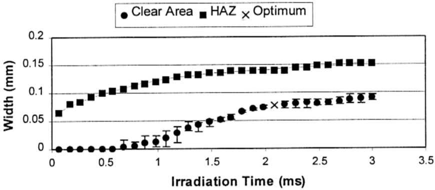


Figure 4.17 (e): Using 5.0 W Argon Ion Laser

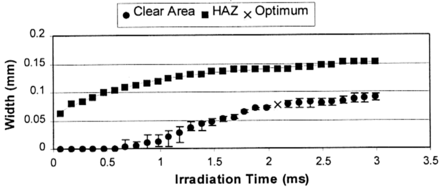


Figure 4.17 (f): Using 6.0 W Argon Ion Laser

Figure 4.18: Width of Clear Area and HAZ as a function of irradiation time for Triacetate film.

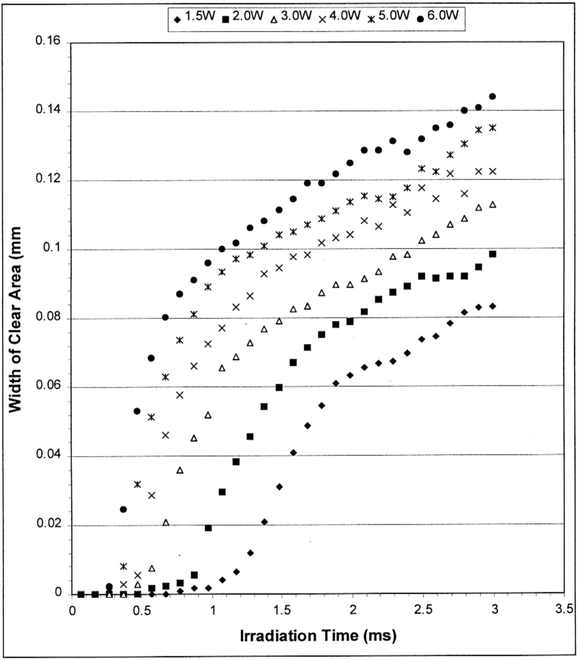


Figure 4.19: Width of Clear Area as a function of irradiation time for Polyester film.

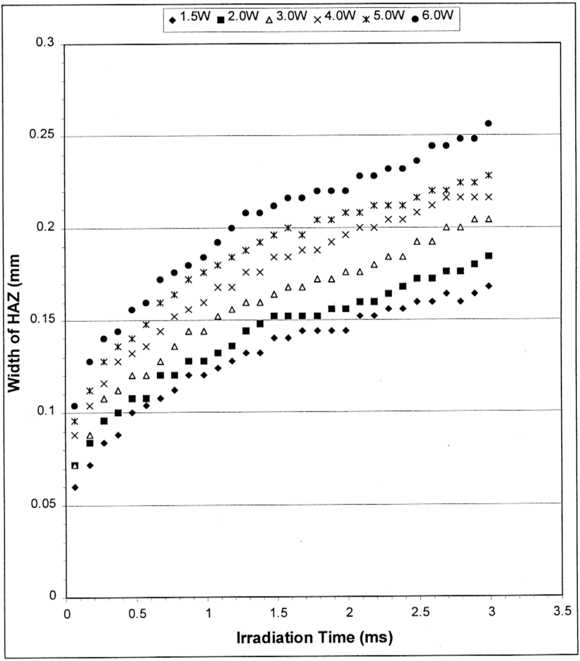


Figure 4.20: Width of HAZ as a function of irradiation time for Polyester film.

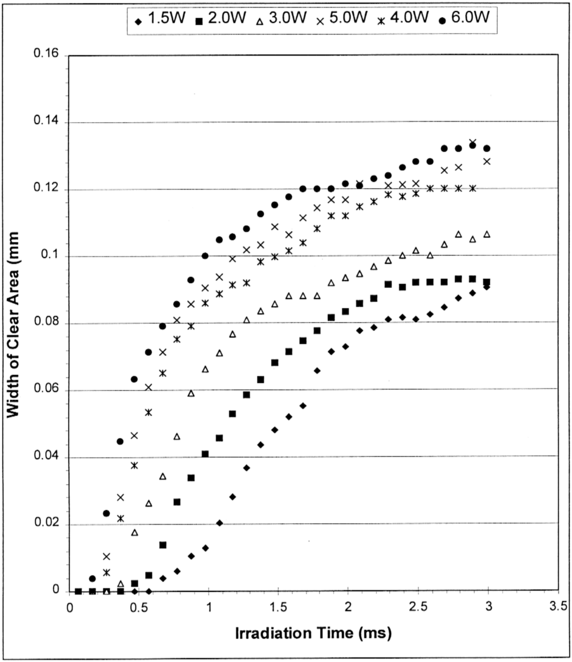


Figure 4.21: Width of Clear Area as a function of irradiation time for Triacetate film.

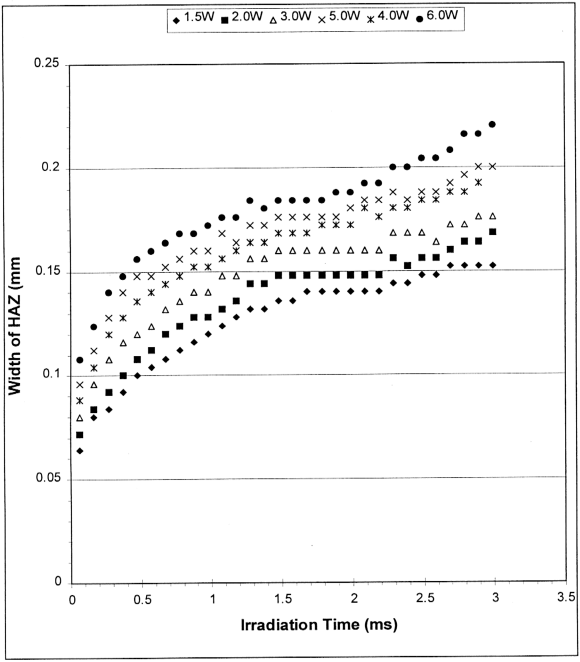


Figure 4.22: Width of HAZ as a function of irradiation time for Triacetate film.

For the various laser outputs, Clear Area only starts to form when the laser irradiation time is sufficiently long to allow the emulsion to absorb enough energy. The width of the Clear Area varies over a wide range in lower scanning time and the variation progressively reduces as more emulsion is removed through vaporisation. At an optimum scanning speed, the width of the Clear Area becomes consistent. At this point, the emulsion removal is almost complete and clean and this represents the best etching quality. Furthermore, the ratio of Clear Area to the HAZ is initially large but converge to about 50% at optimum scanning speed and beyond. At longer scanning time, substrate damage occurs and the width of the Clear Area fluctuates again. The width of HAZ is quite uniform regardless of scanning time.

For Triacetate film, the optimum scanning time is longer but give cleaner line edges. This observation is discussed in Section 4.3.4. Also at longer scanning time, there is less variation in Clear Area of Triacetate film than Polyester film.

As reviewed in Section 2.2, although emulsion's decomposition temperature is higher than Polyester and Triacetate substrate's deformation temperatures, it appears as though the substrates are not thermally affected by the high temperature during the emulsion's vaporisation. This can happen if the laser irradiation time is shorter than heat diffusion time to the substrate layer. At laser irradiation time close to the heat diffusion time, heat conduction may raise the substrate's temperature above its glass transition or melting temperature briefly. But when the emulsion is vaporised and the laser irradiation is terminated, the substrate may resolidify and appear undamaged. At low scanning velocity, there is enough time for significant thermal diffusion and the substrate will undergo thermal decomposition.

4.3.2 Dependence of Optimum Marking Speed on Laser Power

In order to determine what are the optimum parameters to be used while scanning, a set of the best lines marked using different power level is chosen. The best lines are visually inspected and selected based on line consistency and transparency of the Clear Area without visible damage to the substrate. Although the selection process is arguably subjective, nevertheless it gives a good picture of the operating parameter that is needed to create the right type of line. Furthermore, as seen from Section 4.4.1, the optimum lines selected coincide with the point where variation in (largest and smallest) Clear Area's width is minimum and the ratio of Clear Area to HAZ is about 0.5.

Figure 4.23 and 4.24 show the optimum marking speed as a function of laser power. It is seen that the optimum marking speed linearly increases with laser power used. The marking rate is dependent only on the incident laser irradiance.

For Polyester film, the marking rate is about 73 $mm.s^{-1}$ at 1.5 W, and subsequently increasing at the rate of 24 $mm.s^{-1}.W^{-1}$. For laser power of 4.0W, the marking speed is approximately 133 $mm.s^{-1}$. For Triacetate film, the marking rate is about 68 $mm.s^{-1}$ at 1.5 W, and subsequently increasing at the rate of 17 $mm.s^{-1}.W^{-1}$. For laser power of 4.0W, the marking speed is approximately 111 $mm.s^{-1}$.

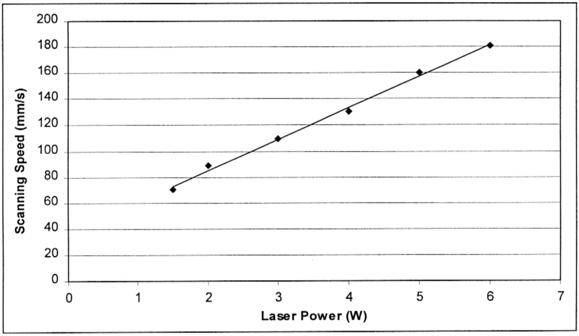


Figure 4.23: Optimum marking speed as a function of laser power for Polyester film.

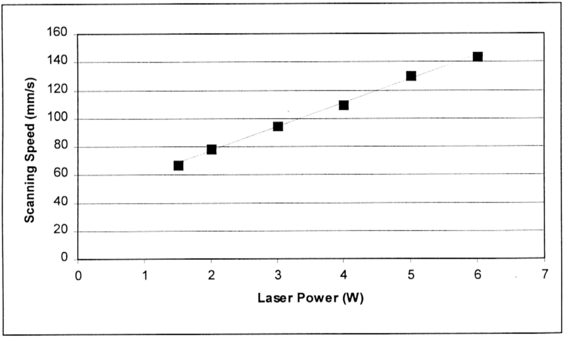


Figure 4.24: Optimum marking speed as a function of laser power for Triacetate film.

Although according to the manufacturer, the emulsion material is the same for both types of film, optimum marking rate on Triacetate film appears to be slower. For Triacetate film, the best lines chosen are of better quality than those from Polyester film because it is possible to obtain cleaner emulsion removal by using a slower marking rate.

4.3.3 Dependence of Optimum Marking Width on Laser Power.

The optimum marking width is based on the same lines selected in Section 4.3.3. Figure 4.25 and 4.26 shows the optimum marking width of the Clear Area and HAZ as a function of laser power. Analysis from the graph shows that the width of both the Clear Area and HAZ linearly increases with laser power used. This may be due to the Gaussian profile beam.

Another reason that the width of Clear Area and HAZ increases with laser power may be explained by heat diffusion. Etching at lower laser power requires slower scanning speed. This allows longer time for heat diffusion. Therefore, some of the absorbed energy may be lost through diffusion to the surrounding emulsion and substrate resulting in small etching width. At higher laser power, the higher scanning speed used allow less time for heat diffusion and therefore the more of the absorbed energy can be used to remove emulsion resulting in increased etching width.

For Polyester film, the optimum width of Clear Area is found to be 65 μm at 1.5 W laser power and increasing at the rate of 7 microns per watt while the width of HAZ is 145 μm at 1.5 W laser power and increasing at the rate of 5 microns per watt.

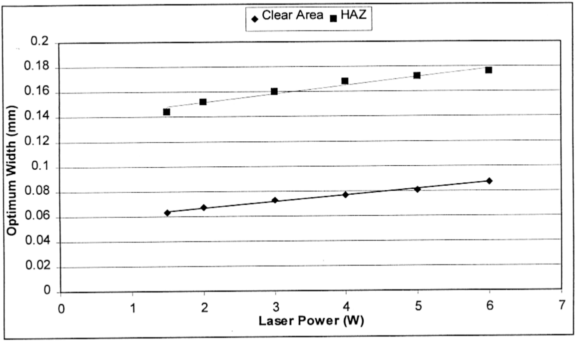


Figure 4.25: Width of Clear Area and HAZ as a function of laser power for Polyester film.

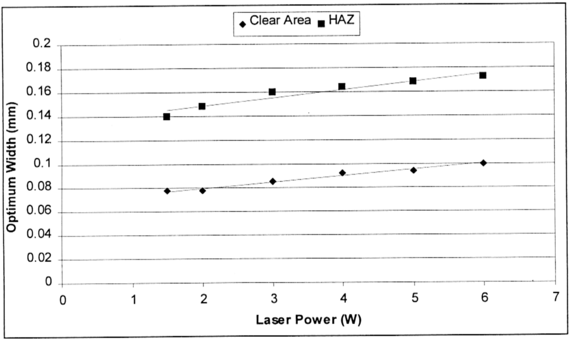


Figure 4.26: Width of Clear Area and HAZ as a function of laser power for Triacetate film.

4.3.4 Dependence of Clear Area Width on Laser Fluence.

Figure 4.27 and 4.28 shows the dependence of the width of Clear Area on laser fluence. The laser fluence is calculated as follows: -

$$\text{Laser fluence} = \frac{P \times t}{\pi w_0^2}\ \text{J/mm}^2$$

where P = laser power (W), t = irradiation time (s), w_o = beam waist radius (mm)

As seen in Figure 4.27 and 4.28, etching begins as soon as a specific threshold fluence (Φ_{th}) is obtained. The width of the Clear Area increases almost linearly over the range of 6 to 10 J/mm^2. The rate of emulsion removal is calculated to be 14 μm/(Jmm^{-2}). This phenomenon is similar to the laser ablation process, where the etching rate, defined as the thickness of the layer ablated per laser pulse, is linearly dependent on the incident fluence [3][14]. The linearity of the etching rate as a function of laser fluence implies that that there is negligible heat diffusion loss and the emulsion vapour stream ejected from the film surface does not absorb significant laser energy.

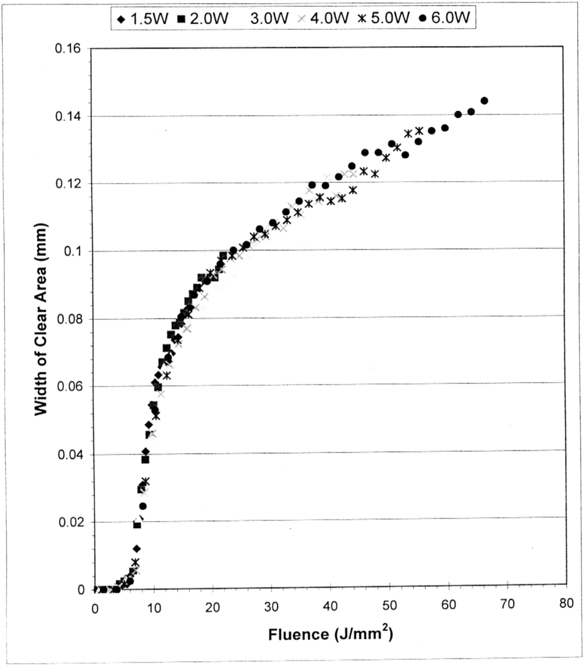


Figure 4.27. The width of Clear Area as a function of laser fluence for Polyester film

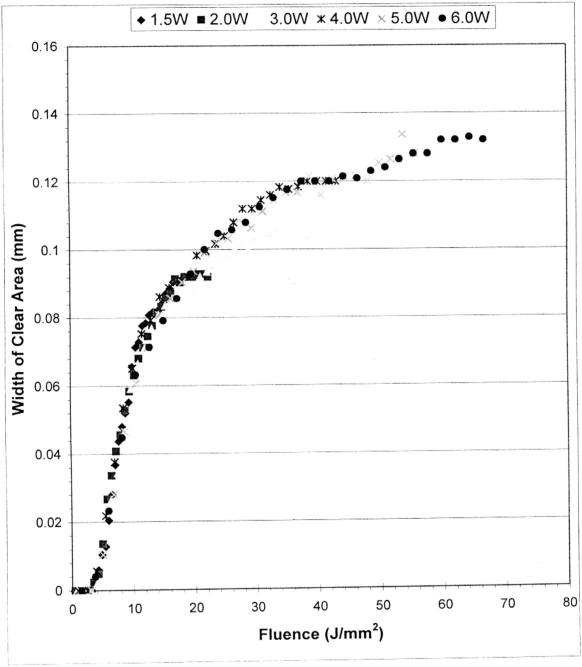


Figure 4.28. The width of Clear Area as a function of laser fluence for Triacetate film

At higher fluence, the profile of the curve starts to levels off. The levelling off of the etch rate may be contributed by the following reasons:

i. At the centre of the line, where the irradiance is the highest, the emulsion layer that absorbs sufficient energy is thermally decomposed and ejected as gas plume. The remaining substrate layer is transparent to the laser beam. Longer exposure to the laser irradiation is useless as the excess laser energy is simply transmitted through the substrate layer. At the same time, the side of the line (where emulsion energy absorption is slower due to lower intensity at the side of the Gaussian beam's intensity distribution) continues to absorb laser energy until they reach decomposition temperature and therefore propagate at a slower rate. This process is illustrated in figure 4.31.

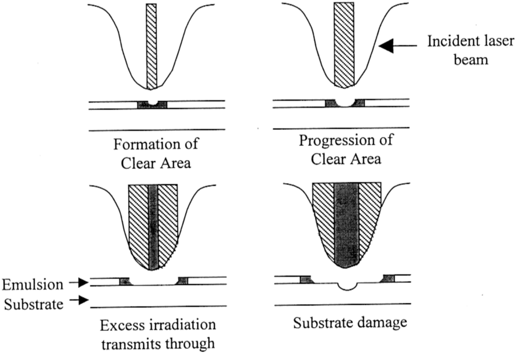


Figure 4.31: Formation and progression of the etching zone.

ii. Part of the absorbed energy may be lost due to heat diffusion into the surrounding emulsion and substrate.

iii. Absorption or scattering of part of the laser pulse by the plume may shield the material deeper in the emulsion from interacting with the laser beam.

It is interesting to note that the optimum marking widths fall immediately after the linear region of the fluence curve. This implies that beyond the optimum marking speed, there is a significant contribution from heat diffusion. As shown earlier, heat diffusion causes reduced optimum marking width at lower laser power.

For both the Polyester and Triacetate film, the emulsion vaporisation threshold fluence is found to be about 4 J/mm^2. This is due to the fact that the same emulsion is used for both types of films.

Figure 4.29 and 4.30 show the dependence of the width of HAZ on laser fluence. The graphs appear to be sharing a similar characteristic S-curve to that of Figure 4.27 and 4.28. However, the graph shows only the non-linear portion of the curve since the fluence at which HAZ begins to form is not known. As seen from the graphs, a large portion of the curve is non-linear. This implies that heat diffusion is very significant. Heat diffusion loss to the surrounding caused slower increase in the width of HAZ when compared to the increase in laser fluence used.

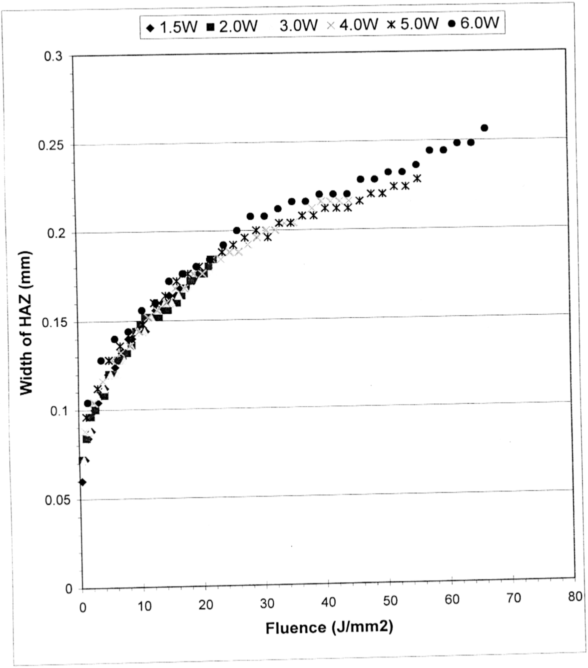


Figure 4.29: The width of HAZ as a function of laser fluence for Polyester film.