NAPIER UNIVERSITY
EDINBURGH

Laser Writable Polymers:
Markability and Durability Characteristics

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A thesis submission in partial fulfilment of the requirements of
Napier University for the award of Doctorate of Philosophy (Ph.D.)

September 2008

AUTHOR DECLARATION

I confirm that work carried out and presented for this dissertation is my own.

1. Where I have consulted the published work of others this is always clearly attributed.

2. Where I have quoted from the work of others the source is always given. With the exception of such quotations this dissertation is entirely my own work.

3. The material presented here has not been previously submitted for assessment as part of any degree.

Satya PK Meruva

ABSTRACT

Characters on computer keyboards are typically printed using one of the two different processes, namely tampographic printing and laser marking. Tampographic printing is time consuming (app. 3-5 mins.), requires skilled workers and employs difficult-to-handle chemicals. On the other hand, the laser marking process is rapid (<1 min.), relatively cheap, avoids the need for chemicals and can be carried out with fewer, less skilled operatives than required for tampographic printing. Data from a keyboard production company indicated that there has been a sudden decline in the percentage (from 60% in 2001 to less than 10% in 2003) of laser marked keyboard users over recent years due to a lack of initial contrast of white characters on a dark plastic and poor durability. Under usual office conditions, characters that are used more regularly e.g. 'e' or 's', can be erased in less than 3-6 months. Further, generating a durable high contrast laser mark on dark coloured polymers has also long been an issue.

The thesis initially reports on an investigation into the reasons for lack of initial contrast and subsequent discolouration of laser marked and tampo printed characters. This is followed by the development of a range of plastics compounds based on ABS and containing a series of different additives. Criteria for selecting additives that would respond appropriately to a laser are also proposed. The compounds were laser marked under a 1064nm Nd:YAG laser at different power, frequency and speed settings. Plaques of the material were manufactured and laser marked in a grid-like pattern to study both the effect of frequency and speed of marking. The mechanisms associated with the laser-material interaction during the marking process were also investigated using light microscopy and scanning electron microscopy. Microscopy was also employed to observe the morphology of the marks left by the laser. Finally a unique test regime was designed to characterise the durability of the laser markings under conditions that attempt to simulate those experienced in practice.

Results show that aluminium trihydroxide generated superior contrast and exhibited enhanced durability characteristics when compared with nine other micro-additives. Nano-additives, such as nano titanium dioxide portrayed better contrast and durability performance when compared to

their micro-size additive equivalents. Analysis of the test plaque results clearly demonstrated that for a specific material compound, it is possible to optimise the laser settings to achieve the best combination of character contrast and durability.

Finally, this work is believed to have made a significant contribution to the rather sparse laser markable polymers research field. It will assist in the development of a more fundamental understanding of laser/material interactions and provide a basis for future work in optimising materials formulations for successful laser marking.

ACKNOWLEDGEMENTS

My Parents, Friends and Family have been my inspiration and a great driving force to study and complete my work. Mrs. Nirmala & Mr. Lakshmi Narayana (Parents), Mrs. Suvarna & Mr. Satish Avala and Mr. Harish Kumar have been and are an everlasting source of energy and power to support me to achieve my goals and ambitions.

I would like to thank my supervisor Dr. Mike B Barker, Reader in Polymer Engineering for his encouragement and incessant support through out the work. I am deeply grateful to him for being the torch bearer and also giving me the strength and motivation whenever necessary.

Thanks to Dr. Janos Hajto for his knowledge and support for trying to overcome various obstacles during the process of work. Also thanking Mr. Colin S Hindle, Mr. Alan Davidson and Mr Randall Claywell for their valuable suggestions during the course of the work is spontaneous.

I would like to thank Mr. Bill Brownlee and Mrs. Lynn Chalmers, for their invaluable help and support all throughout the course of the work in the laboratory. Thanks to Napier University, Edinburgh for providing the necessary infrastructure and laboratory facilities to complete the work. Kindest regards go to Thinklaser Services and Systems for providing laser marking services which has been an important part of the work. Regards to NMB Minebea UK Limited for collaborating with the University for the research.

I have an endless list of friends, well-wishers and mentors who made me, ME. To name a few- Kalyan Tungala, Doondy Rangu, Rajesh Reddy Yedla, Manoj Voona, Rajesh Gavini, Ajay Mandava, Revanth Ravipati, Raghunath Kantamaneni, Parandham Vemulapalli, Ravi Kiran Chigurupati, Sravanthi Potluri, Vijay Veermachaneni, Anil Dondapati, Anil Bodapati, Pavan Kusam, Rama Gopal Appalla, Surya Kiran Veluvolu, Satish Garapati, Devaki Rani, Swathi Behara and the list goes on and all of them have been of immense support to me at various stages and phases of my life. Thanking them may be will demean our relationship.

Dr. Bhargava NRMR has been a great inspiration, my role model and one of the key reasons for my interest towards research. Thanking him from my heart, for igniting the passion, is unprompted.

Last but not the least, I would like to finally acknowledge one and all who have directly or indirectly co-operated in the successful completion of the work.

Satya Meruva...

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LIST OF ABBREVIATIONS

Acronym	**Abbreviation**
ABS	Acrylonitrile Butadiene Styrene
Nd:YAG	Neodymium: Yttrium Aluminium Garnet
UV	Ultra-Violet
SEM	Scanning Electron Microscope
EDXA	Energy Dispersive X-ray Analysis
Ag	Silver
PTFE	Poly Tetra Fluoro Ethylene
GTD	Grey Tampographic Dell
BTL	Black Tampographic Logitech
BTP	Black Tampographic Laptop
BTI	Black Tampographic IBM
BeLB	Beige Laser Bell
BeLL	Beige Laser Logitech
BLD	Black Laser Dell
BLN	Black Laser NMB
T	Titanium dioxide (TiO_2)
A	Aluminium trihydroxide (Al_2O_3 $3H_2O$)
AZ	Azodicarbonamide
F	Iron oxide(Fe_2O_3)
SG	Sliver Coated Glass

Acronym	**Abbreviation**
MV	Micafil (Vermiculite)
MP	Phlogopite Mica
MM	Muscovite Mica
B	Bone Char
S	Silicon (Si)
NT	Nano Titanium dioxide
NZ	Nano Zinc oxide
NC	Nano Copper oxide
IR	Iriodin (Merck's compound)
NMB	NMB compound
AT	Aluminium trihydroxide + Titanium dioxide
AF	Aluminium trihydroxide + Iron Oxide
AS	Aluminium trihydroxide + Silicon dioxide
BA	Bone Char + Aluminium trihydroxide
SA	Silicon dioxide + Aluminium trihydroxide
BT	Bone Char + Titanium dioxide
ST	Silicon dioxide + Titanium dioxide
ΔE	Difference in Contrast
P60F25	60% Power; 25MHz Frequency setting for laser marking
Grid Marking	Grid-like pattern laser marking

1.0 INTRODUCTION

1.1 Background

The research was initiated by NMB Minebea UK Limited, a company based at Inchinnan Business Park Glasgow. They are global manufacturers of power supplies, electrical products and also finish computer keyboards by printing characters onto keycaps. Employing dark coloured computer peripherals instead of the traditional beige coloured casings, to improve the aesthetics and give a professional look, is the background for this work. Generating dark coloured characters with good contrast and durability on light/beige coloured keycaps is well established. However, generating a light coloured mark with the similar levels of contrast and durability on a dark coloured background is a challenging task.

Marking on the keyboard is normally carried out in two different ways- Tampographic printing or Laser marking. Tampographic printing involves chemicals and uses silicon rubber pads to deposit ink on the keyboard. The process is labour intensive, time consuming and the characters are further coated with an ultra-violet (UV) curable resin to improve durability performance.

Laser marking uses equipment with specific wavelength and power density to produce a mark/character on the keyboard. Characters are generated in a single step with out the requirement of skilled labour, thus making laser marking process fast and efficient. These advantages combined with its versatility makes laser marking the process of choice when printing characters onto computer keycaps.

1.2 Reasons for Research

Figures from NMB indicate that in 2002 approximately 3.5 million keyboards were sold, out of which 60% were laser marked. But in 2003 90% of the keyboards sold were tampographic printed[1,2]. Feedback from customers indicate the reason for this significant reduction in the number of laser markable keyboards is because:

- the light coloured laser mark lacked contrast against the dark coloured background
- discolouration of the printed characters occured after only a few months use

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[1] Meruva, S., Quality and Durability of Characters on Computer Keycaps, in School of Engineering. 2003, Napier University: Edinburgh.
[2] Campbell, A. M., Visual Aids for Keyboard Printing Processes. 2002, NMB Minebea UK Ltd.: Glasgow.

Investigating into the reasons for poor contrast and subsequent discolouration of the laser marked characters is the basis for the work, followed by working to improve the contrast and duribility is the main part of this research.

1.3 Aims of the Work

The main aims of the work are to:

I. Investigate the laser-material interaction on commercially available computer keyboards to determine the reasons for lack of initial contrast and durability of printed characters
II. Generate a light coloured laser mark on the underlying dark coloured keycap by
    a. Developing novel combinations of speciality grade plastics using a range of different additive systems
    b. Understanding the laser-material interaction on newly developed materials when laser marked at different settings
III. Design a test regime which simulates practical conditions to determine the performance of keycaps made with these new material formulations

1.4 Achieving Aims of the Work

Compounding & Marking

Production of various compounds, with Acrylonitrile Butadiene Styrene (ABS) as the base polymer and a range of different additives, using the Brabender compounding machine followed by laser marking the plaques under an Nd:YAG (Neodymium:Yttrium Aluminium Garnet) laser is the main body of the work.

Durability Tests

Determining the life of printed characters on keycaps by performing a series of wear tests specifically designed to simulate practical working conditions is fundamental. The tests include a combination of factors such as the effect of light from natural or artificial sources, wear caused by the friction between the finger and the character along with effect the sweat secreted while typing.

Microscopy

Examination of the laser marked samples is carried out under the Scanning Electron Microscope (SEM) to understand and determine the marking pattern of the character with good durability. Microscopic examinations were carried out after the samples were subjected to durability tests, in order to understand and record the difference in the printed characters before and after the tests.

1.5 Outline of the Report

In Chapter 1, background research along with the reasons for pioneering the research are expalined. Aims and objectives of the work are described in this chapter.

A systematic review of the literature, carried out to acquire a thorough understanding of the research area, is undertaken in Chapter 2.

Various experimental techniques employed to achieve the set aims are described in Chapter 3 along with the different materials used for carrying out the experiments.

Discussing the results obtained from the various experiments carried out is the vital part of the thesis which is divided into three parts and clearly presented in Chapter 4 for an easy understanding.

Finally, the main conclusions of the research are listed in Chapter 5 followed by innovative and new ideas for future work.

2.0 LITERATURE

2.1 Marking Polymers

Polymers or computer keyboards are printed in two ways. Namely,

- Tampographic printing and
- Laser marking

2.2 Tampographic Printing

Printing characters on computer keyboards with ink is called Tampographic printing or Pad printing. Tampo printing can be produced on a variety different materials with stroke widths as fine as 0.076mm width, with considerable accuracy and reproducibility. The four colour process allows it reproduce all the colours in the spectrum with use of four primary colours. Also, the wet-on-wet printing technology permits the printing of second colour immediately after the first print because of the use of instant dry inks. The print process involves chemicals in the form of ink which is transferred to the keyboard, makes the process lengthy, time consuming and energy inefficient. This process is similar to the offset printing mechanism, the only difference being the former is done on paper and the latter on polymers.

Pad printing uses a series of soft and spongy silicon rubber pads, to carry ink from a pool to the keyboards. These inks are 4-6μm thick which contain 20% pigments and fast evaporating agents. So, a cooling mechanism is necessary to control the temperature and regulate humidity of the printing process, which adversely affects the viscosity of the liquid ink and hence the process[1]. Parts printed need high surface energy than the silicon pad and some of the parts require pre-heating for ink transfer to take place.

Keyboards are placed in between jigs for a firm support while printing, which is done in 2-3 stages depending on its complexity and curvature. Figure 2.1 shows a clear pictorial view of the Tampographic printing process[2]. The printed characters are further coated with a ultra-violet (UV) solution which is cured under a strong UV light at 35-40°C for specific amount of time to

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[1] Meruva, S., Quality and Durability of Characters on Computer Keycaps, in School of Engineering. 2003, Napier University: Edinburgh.

[2] Campbell, A. M., Visual Aids for Keyboard Printing Processes. 2002, NMB Minebea UK Ltd.: Glasgow.

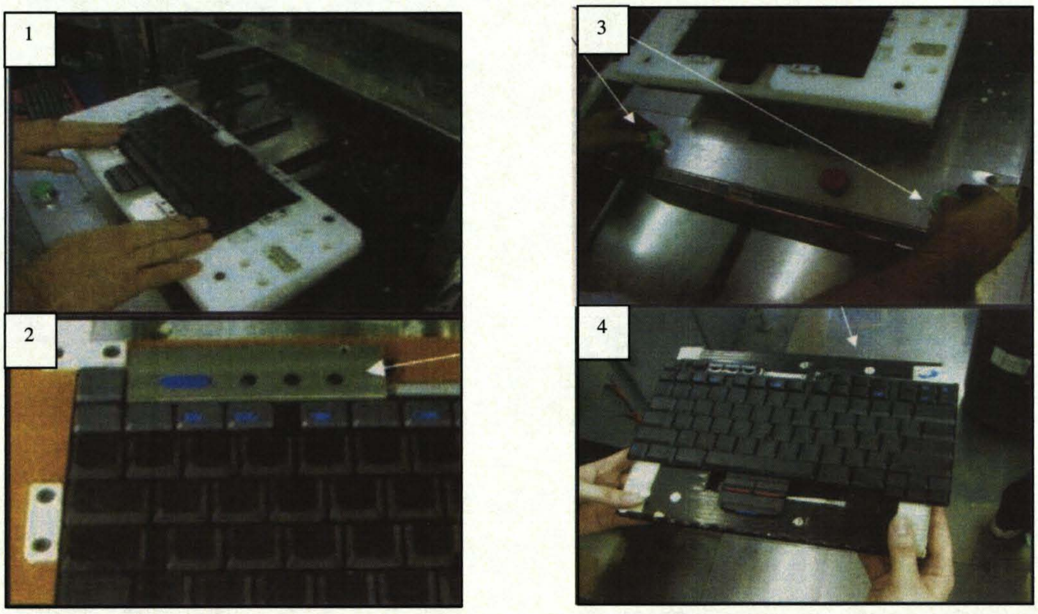
improve life or durability performance of the keycaps. Images of UV coating and curing stages are shown in figure 2.2[2].

2.2.1 Advantages of Tampographic Printing

The advantages of tampographic printing are:

- Good contrast marks on a variety of different materials
- Four colour process, enables reproduction of all the colours from a spectrum
- Characters with improved life or good durability
- Effect of external (natural or artificial) light sources is minimum
- Effect of sweat on the printed characters is low

The above advantages of the tampographic printed are primarily due to the protective UV coating applied over the printed characters.



1. Place the Keyboard in the Tampo-print fixture.
2. Make sure the keyboard is flat and sits exactly in the jig.
3. Press both green buttons at the same time to move the base and activate printing.
4. Remove keyboard from jig and pass to next operation.

Figure 2-1 Tampo printing process[2].

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[2] Campbell, A. M., Visual Aids for Keyboard Printing Processes. 2002, NMB Minebea UK Ltd.: Glasgow.

2.2.2 *Disadvantages of Tampographic Printing*

The disadvantages of Tampographic printing are:

- It is a lengthy and time-consuming process (≈ 3-5 minutes)
- It is a difficult process and highly skilled labour is necessary for minute adjustments
- Tooling costs and regular maintenance prove to be expensive (≈ £100,000-£150,000)
- Reproducibility is moderate and printing can be done only on plain surfaces
- Use of chemicals (inks) causes environmental pollution
- Pre-heating of the substrate to transfer inks in certain cases with low surface energy than the silicon pads
- Difficult to print on small articles or on large objects

1. Place the Keyboard into the fixture and ensure the keyboard is flat and sits exactly in the jig.
2. Press both green buttons at the same time to move the base and activate Ultra-Violet coating.
3. Remove keyboard from jig and place it into the Ultra-Violet dryer.

Figure 2-2 Ultra-violet coating process[2].

2.3 Laser Marking

In 1960 the first laser (Light Amplification Stimulation Emission Radiation) took shape, since then work has been carried out around the world to improve the types of laser, power output and its range of applications. Lasers can now be seen in many fields, e.g. industry, research and development, education, agriculture and military. Monochromaticity, coherence, good directionality, high brightness and short pulse duration are the five key properties which led to the rapid development of lasers. Carbon dioxide (CO_2) laser, Nd:YAG laser and Excimer laser are some of the widely used and important for plastics marking industry[3].

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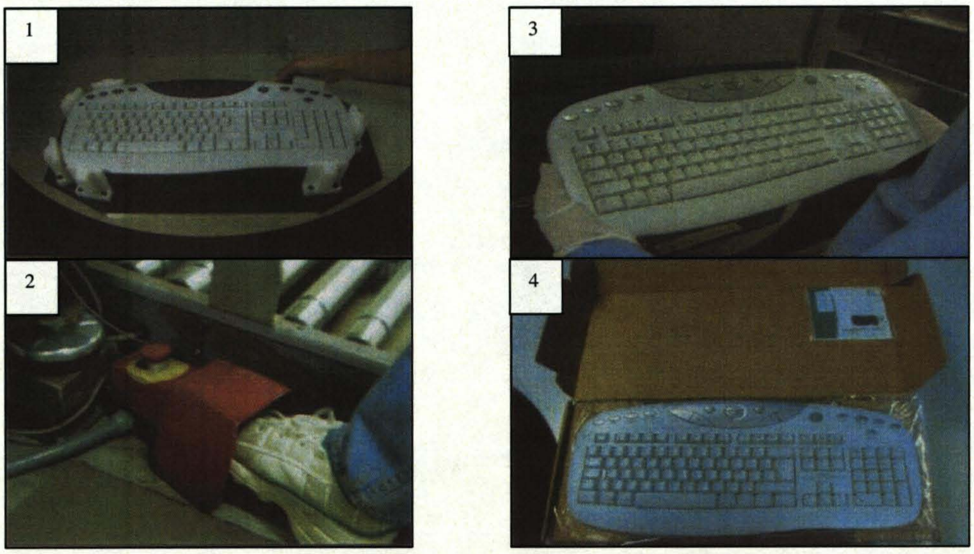
[2] Campbell, A. M., Visual Aids for Keyboard Printing Processes. 2002, NMB Minebea UK Ltd.: Glasgow.

[3] Laser Marking Technologies 2002, www.sintecoptronics.com visited in September 2004, Sintec Optronics Pte. Ltd.: Singapore.

Laser marking is a surface process which includes one or more of the following processes for marking the characters[3]:

- Black Carbonisation
- Bleaching
- Physical modification of the surface finish
- Scribing a shallow groove into the material by vaporisation
- Highly controlled modification of the surface by melting

Keyboard marking is a simple single step process. The keyboard is held in between guards on a rotatable table, which moves into the machine and marking is completed in a few seconds.
Images of various stages involved in laser marking process are shown in figure 2.3[2]. Measuring the quality of the printed character is very important and is determined using specialised wear testing equipment. A photograph showing a typical laser marking procedure is shown in figure 2.4[4].



1. Place the Keyboard in the Laser marking machine
2. Make sure the keyboard is flat and sits exactly in the jig and press the Laser foot pedal
3. The turn table rotates into the machine and marking is completed
4. Inspect the quality of print characters and place in the carton

Figure 2-3 Photographs showing the laser marking process[1].

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[1] Meruva, S., Quality and Durability of Characters on Computer Keycaps, in School of Engineering. 2003, Napier University: Edinburgh.

[2] Campbell, A. M., Visual Aids for Keyboard Printing Processes. 2002, NMB Minebea UK Ltd.: Glasgow.

[3] Laser Marking Technologies 2002, www.sintecoptronics.com visited in September 2004, Sintec Optronics Pte. Ltd.: Singapore.

[4] Laser Marking Technology - White Paper, www.advanced-input.com visited in January 2004, Easterline, Advanced Input Systems: USA.

2.3.1 Advantages of Laser Marking

Laser marking offers many advantages like:

- Marking with laser is generally permanent with high quality
- Low operating expenses due to reduced or no tooling costs
- No direct contact between tool and the work piece
- No special environment is required and less environmental pollution
- Easy automation and integration into the production line
- Efficient marking at high speeds (< 1 minute) and enhanced reproducibility
- Accurate marking is produced even on irregular surfaces

Figure 2-4 Laser marking process[4].

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[4] Laser Marking Technology - White Paper, www.advanced-input.com visited in January 2004, Easterline, Advanced Input Systems: USA.

2.3.2 Disadvantages of Laser Marking

In spite of its numerous advantages, the application of laser marking is limited due to the following disadvantages:

- Less contrast is obtained and discolouration effects are seen only in the case of plastics.
- High capital investment – but increased productivity, reduction in the inventory cost, improved quality and long term ownership make it economical.

2.4 Differences between Tampographic printing and Laser marking

Property	**Tampographic Printing**	**Laser marking**
Cost[7]	Less capital (£40,000) Annual Consumables i.e. chemicals etc. (£12,500-£22,500) Total Plates costs & Intangible cost (£90,000-£125,000)	More capital (£30,000-60,000) Annual Consumables incl. Water and Electricity (Less than £3,500) No Plates costs & Intangible cost (£0)
Speed	Time consuming 3-4 stages Low production rates	Very quick Single stage High production rates
Quality	Good Contrast Less discolouration Moderate accuracy Moderate reproducibility More losses	Moderate contrast and chances for discolouration (in case of plastics only) Very accurate High reproducibility More efficiency
Misc.	Skilled labour required Direct contact between tool and work piece Difficult to automate and integrate Not environmental friendly Can be done only on flat surfaces	Skilled labour not required No direct contact between the tool and the work piece Easy automation and integration Free from contamination Can be done on any surface

Table 2.1 Differences between Tampographic and Laser marking process[1].

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[1] Meruva, S., Quality and Durability of Characters on Computer Keycaps, in School of Engineering. 2003, Napier University: Edinburgh.

[7] Laser Marking on Plastics Materials, www.rofin-basel.com visited in January 2004, Rofin-Basel, USA.

2.5 Factors Influencing Marking

As discussed in earlier sections, laser marking dark coloured plastics to generate a light coloured mark is a challenging task. Contrast and durability of the laser mark are influenced by the following factors:

- Laser Technology and Marking
- Material Selection

2.6 Laser Technology and Marking

2.6.1 Types of Laser

Lasers typically generate light using an energy source, a lasing medium that allows the light to concentrate and the reflective mirrors direct the energy to the object to generate a laser mark. Plastics are marked using three different types of laser namely,

- Carbon dioxide (CO_2)
- Excimer
- Nd:YAG

TEA- CO_2 Laser

A Transversal Excited Atmospheric (TEA) -Carbon Dioxide Laser operates at a relatively long wavelength of 10,640nm and as the name suggests uses CO_2 as the lasing medium. The intense laser light is passed through a mask that has the information etched on to it which is reflected and redirected on to the object. The resultant mark, shown in figure 2.5, is achieved by partial carbonisation of the polymer with a depth typically in the range of 100-500μm.

Table 2.2 shows the mechanism of laser marking for different types of lasers at various wave lengths. Applications of CO_2 laser marking include simple coding such as numbering and the quality of the laser mark is comparable to the dot matrix print[5-8].

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[5] Mulholland, B.M., A Report on Laser Markable Engineering Resins, www.ticona.com visited in March 2004, Ticona, USA.

[6] Technical Information on Laser Marking 2001, www.trumpf.com visited in November 2005, TRUMPF Laser Marking Systems AG, Germany

[7] Laser Marking on Plastics Materials, www.rofin-basel.com visited in January 2004, Rofin-Basel, USA.

[8] Sabreen, S.R., of High Speed Colour Laser Marking of Plastics, in Plastics Decorating Magazine 2005, Peterson Publications.

Figure 2-5 CO_2 laser marked character[8].

Laser	Wavelength	Type	Mechanisms
Excimer	196nm 248nm 308nm	Mask	Photochemical ablation (high-precision)
	352nm		Photochemical reaction (bleaching of colours)
Nd:YAG (freq. doubled)	532nm	Stroke	Photochemical reaction (bleaching of colours)
Nd:YAG	1064nm	Stroke	Thermo chemical reaction (colour change, foaming, engraving, sublimation)
CO_2	10640nm	Mask Stroke	Thermo chemical reaction (melting, vaporizing, engraving)

Table 2.2 Laser-material interaction mechanisms for different lasers and wave lengths[7].

Excimer Laser

The term excimer is short of excited dimer which generates light in the UV range. Wavelength of the excimer laser depends on the molecules, which are typically noble gas halides, ranges between 193-351nm. The laser mark is produced by a photochemical process to generate a dark coloured mark on a light coloured substrate, filled with TiO_2 or other mineral fillers. Even though the mark is only 40μm in depth, the applications are quite limited due to its high capital costs compared to the other lasers and its ability to produce only a dark mark on light substrates[5, 6].

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[5] Mulholland, B.M., A Report on Laser Markable Engineering Resins, www.ticona.com visited in March 2004, Ticona, USA.

[6] Technical Information on Laser Marking 2001, www.trumpf.com visited in November 2005, TRUMPF Laser Marking Systems AG, Germany

[7] Laser Marking on Plastics Materials, www.rofin-basel.com visited in January 2004, Rofin-Basel, USA.

[8] Sabreen, S.R., High Speed Colour Laser Marking of Plastics, in Plastics Decorating Magazine 2005, Peterson Publications.

Nd:YAG Laser

Neodymium doped Yttrium Aluminium Garnet (Nd:YAG) is the lasing medium in the Nd:YAG laser which produces laser light at 1064nm. The YAG laser at 1064nm creates a mark by melting and foaming the polymer surface at a depth of 50μm. Laser parameters like frequency and power can be adjusted to produce a mark with good contrast depending on the colour of the base material. The frequency doubled 532nm Nd:YAG green laser which typically affects the pigments or the other additives, through a photochemical reaction shown below, create a high contrast laser mark. YAG lasers flexibility to suit various applications and its ability to interface with computers to generate graphics are some of the reasons for its increasing popularity [5, 6].

Photochemical Reaction

Laser Markable Compound + Laser Energy → White laser marked compound + Gas Occlusion
(Base Material + Additive) **(hv)** **(Foam)**

2.6.2 Introduction to the Nd:YAG laser

Nd:YAG is a crystal used as an active lasing medium in a solid state laser. Triply ionised Nd is the dopant which replaces Yttrium in the $Y_3Al_{15}O_{12}$ crystal, since they have the same ion size and forms the Nd:YAG crystal[9]. Figure 2.6 shows the crystal structure of YAG at the boundry with Nd[12]. Excitation of the Nd ions to higher energy levels is carried out using external sources and the primary transitions are shown in figure 2.6. Absorption of pumped energy is predominantly at 0.73 & 0.8μm, which decay at meta-stable $^4F_{3/2}$ and $^4I_{11/2}$ levels to produce the required population inversion. This produces a monochromatic and coherent beam of light which is further amplified and oscillated with the use of mirrors to produce the strongest Nd line at 1064nm and only 20-30% of the laser light exits through the laser cavity which is used as the marking tool.

Excitation of the Nd Laser

As stated earlier Nd atoms have to be excited with external sources and this is achieved by Lamp or Diode pumping techniques.

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[5] Mulholland, B.M., A Report on Laser Markable Engineering Resins, www.ticona.com visited in March 2004, Ticona, USA.

[6] Technical Information on Laser Marking 2001, www.trumpf.com visited in November 2005, TRUMPF Laser Marking Systems AG, Germany

[9] Hecht, J., Laser Guidebook. 2nd ed. 1992: McGraw-Hill Publications Inc., Page no. 20-57 & 389-417.

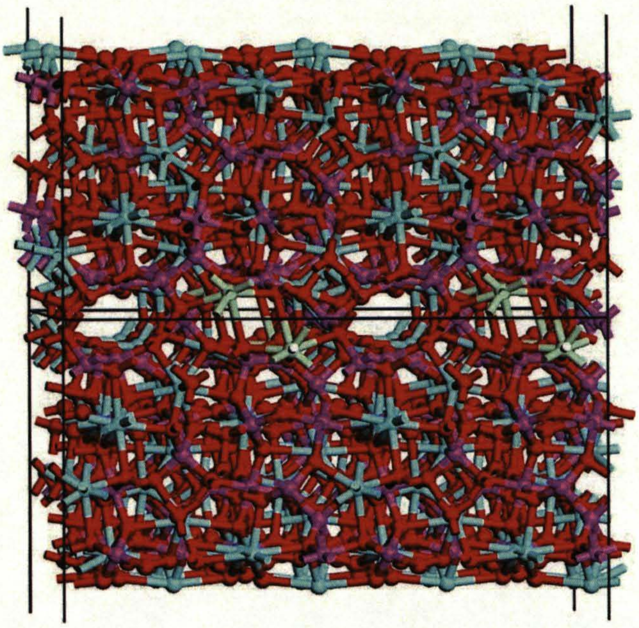

Figure 2-6 Cubic Crystal Structure of YAG at the boundary with Nd[12].

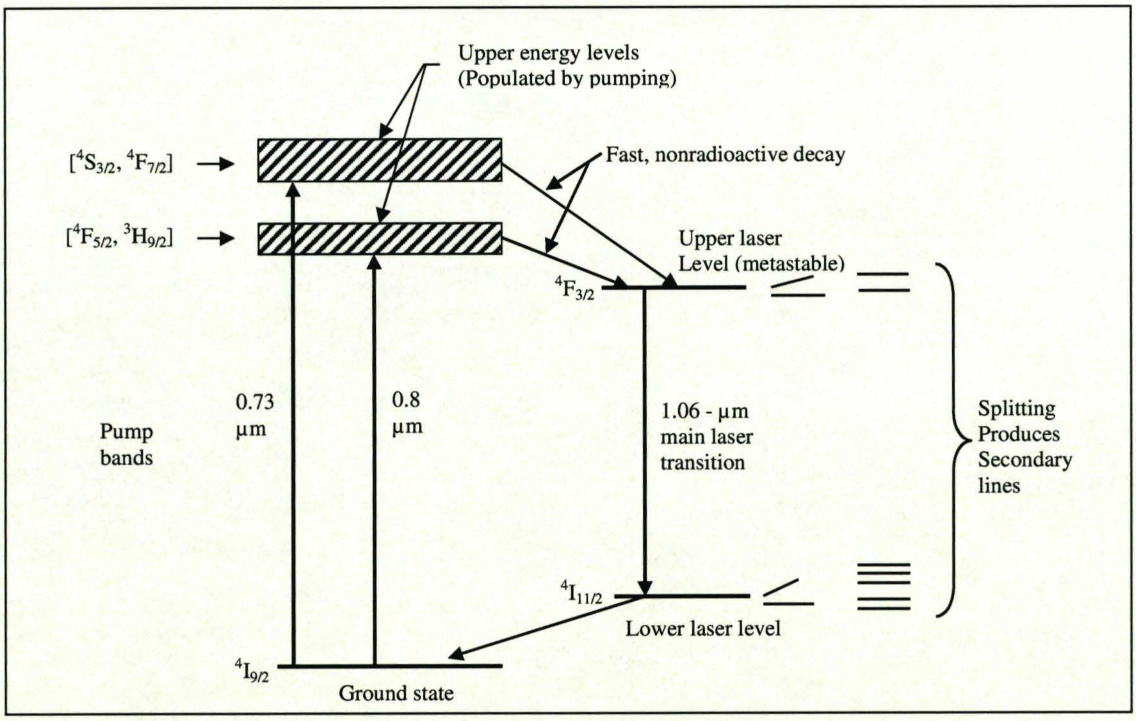

Figure 2-7 Simplified form of the Nd:YAG excitation levels[9].

Lamp Pump Excitation

Broad spectrum light sources like continuous Tungsten arc lamps, Krypton arc lamps or pulsed flash lamps are used for pumping. Even though the lamps emit light over a wide range of wave lengths and offer high intensity, only a narrow range is used for excitation thus making it an inefficient process. The unwanted or the excess light adds to unnecessary heating of the rod which is constantly flushed with external cooling water and hence complicates the process[6, 9].

Diode Pumping Excitation

Semiconductor laser diodes emit laser light with uniform wavelength, a characteristic of the diode, which is used to selectively excite the lasing medium. Table 2.3 compares the laser pumped and diode pumped solid state lasers and confirms the benefits of using a diode pumped solid state laser, shown in figure 2.7, which is better than its competitor.

Diode laser pumping from the end of the rod, as shown in figure 2.7, is a procedure standard at lower power levels which rapidly diverges the beam from the diode laser to fill as much space as possible in the crystal and generate an ultra high quality output beam[6, 9].

Specification	Lamp Pump YAG	Diode Pump YAG
Wavelength	1064nm	1064nm>
Raw Power	10-100 Watt near TEM_{00}	10-100 Watt MM
Power with Best Quality Output	1-22 Watt near TEM_{00}	1-22 Watt TEM_{00}
Beam quality mode	MM to near TEM00	MM to TEM_{00}
Spot Size	Focus lens, Upcollimator and Mode dependant	Focus lens, Upcollimator and Mode dependant
Laser Pump Source Life	400-600 hours	8,000-10,000 hours
Pump Source Replacement Cost	£25-£50	£6,000-£7,500
Laser System Size	Large	Large to Small
Operating cost annual	£1,600	$2,000
Initial laser cost	£24,000 – 30,000	£30,000 - £37,500

Table 2.3 Comparison of lamp and diode pumped Nd:YAG lasers[9].

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[6] Technical Information on Laser Marking 2001, www.trumpf.com visited in Nov. 2005, TRUMPF Laser Marking Systems AG, Germany.
[9] Hecht, J., Laser Guidebook. 2nd ed. 1992: McGraw-Hill Publications Inc., Page no. 20-57 & 389-417.

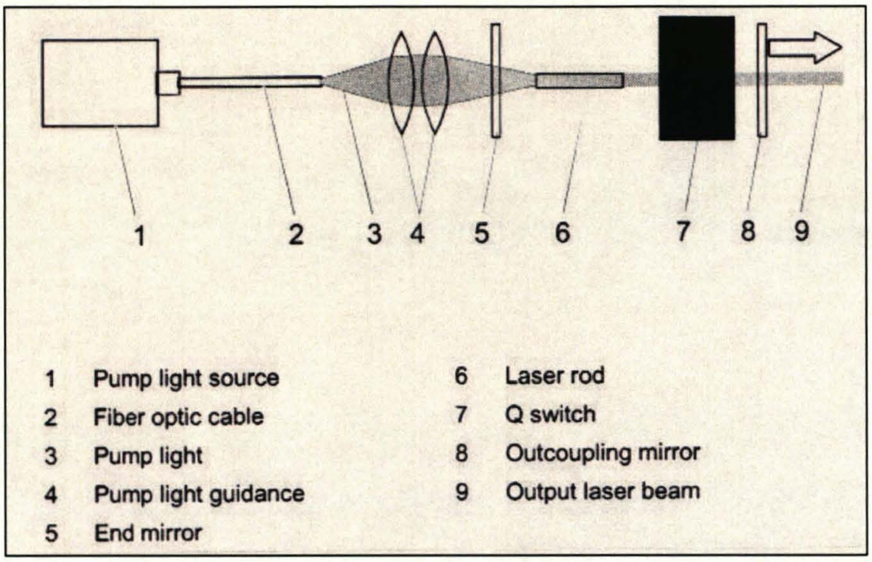

Figure 2-8 Schematic diagram of diode pumped solid-state laser[6].

TEM_{00} & MM

TEM mode is the Transverse Electromagnetic Mode, which is indicated by a two letter index, TEM_{pl}, p is the number of radial zero fields and l is the number of angular zero fields. With $p=l=0$, the TEM_{00} mode is the lowest order, or fundamental transverse mode of the laser resonator in a cylindrical geometry. MM indicates a multi mode type of beam generation by the laser[9].

Q Switch

The Q factor is defined as the ratio of energy stored per pass to the amount of energy dissipated per pass and modulating the Q factor raises interesting possibilities. If the Q factor is kept artificially low, by introducing a lossy optical element, then the energy will gradually accumulate in the laser medium and when the lossy element is removed suddenly huge power bursts of light is produced in which the energy is emitted, for a short period. This rapid change in cavity Q is Q switching.

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[6] Technical Information on Laser Marking 2001, www.trumpf.com visited in Nov. 2005, TRUMPF Laser Marking Systems AG, Germany.

[9] Hecht, J., Laser Guidebook. 2nd ed. 1992: McGraw-Hill Publications Inc., Page no. 20-57 & 389-417.

Q-switching is a technique by which a laser can be made to produce a pulsed output beam. It allows production of extremely high peak power pulses, much higher than would be produced by the same laser if it were operating in a continuous wave (constant output) mode. Q-switching can produce lower pulse repetition rates, higher pulse energies, and much longer pulse durations and some a combination of these can be used to replicate the desired output[9].

Beam Characteristics

The output wavelength of Nd:YAG is close to 1064nm but factors such as interaction between Nd ions and host material can shift it by 1%. Harmonic generation multiplies the frequency by a factor of 2, 3 or 4 by passing the fundamental wave length through non-linear crystals which generate green laser light with wavelengths of 532, 335 and 266nm respectively. Frequency doubled or tripled Nd:YAG lasers are also used for marking plastics[9].

2.6.3 Laser Marking Parameters

Selection of the laser marking parameters is vital to generate a high contrast mark and they depend on the material composition[6, 9]. These factors are:

- Laser power
- Pulse frequency
- Speed of marking
- Focus position and diameter
- Beam quality

Laser Power

Increase in laser power assist in stronger interaction with the material[9]. The excitation energy regulates the intensity of the pumped light and thus the output laser power, making it easily adjustable.

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[9] Hecht, J., Laser Guidebook. 2nd ed. 1992: McGraw-Hill Publications Inc., Page no. 20-57 & 389-417.

Pulse Frequency

Pulse frequency is the duration of a pulse and its consequent pulse peak power. They determine the amount of energy to be applied on a work piece. Different results are obtained depending on the pulse frequency, for example Engraving, Material removal or Colour change.

Speed of Marking

Speed of marking is one of the variables in the work and is set according to the pulse repetition frequency. Figure 2.8 shows the marking pattern at different speeds at a constant pulse frequency.

Focal Position & Focus Diameter and Beam Quality

These three factors are generally optimised with the laser equipment and the material used for marking. Modifying these parameters would unnecessarily increase the scope of the laser material interaction studies and hence are left unaltered. Focal length determines the focus diameter and the marking field size. Beam quality is the beam parameter product 'q' which is a measure of the beam quality and focussability. The smaller the 'q' the better the beam quality and better the ability to focus and produce a fine small diameter. This affects the line thickness and further the speed of marking.

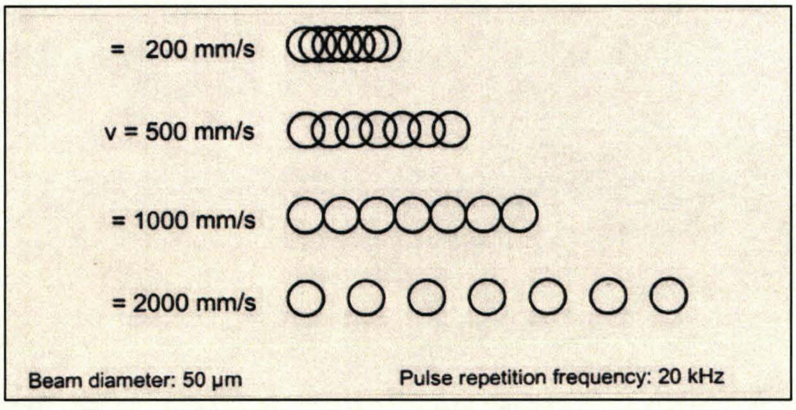

Figure 2-9 Marking patterns at different marking speeds[6].

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[6] Technical Information on Laser Marking 2001, www.trumpf.com visited in Nov. 2005, TRUMPF Laser Marking Systems AG, Germany.

[9] Hecht, J., Laser Guidebook. 2nd ed. 1992: McGraw-Hill Publications Inc., Page no. 20-57 & 389-417.

2.6.4 Laser-Material Interaction

Laser specified by a typical wavelength and high power density is focussed on the material for marking. The type of mark produced during laser-material interaction depends on:

- The type of base material used for marking
- Wavelength of the laser
- Marking parameters of the laser

Depending on these factors laser-material interaction produces the mark in one of the following ways:

Colour Change

In this technique, the material and laser wavelength are selectively optimised to generate a laser mark through colour change of an additive or a dye in the base material. A photograph of the laser marked character by colour change mechanism is shown in figure 2.9[3, 6].

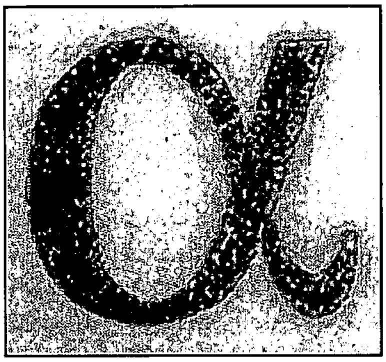

Figure 2-10 Photograph showing the Colour change mechanism[6].

Material Removal

Removing a thin coated layer using a high power laser produces the mark on a multi-layer coated plastic. The coated layer is laser sensitive and is of an entirely different colour from the base material and is removed by the laser to produce a sharp image with high contrast, as shown in figure 2.10[3, 6].

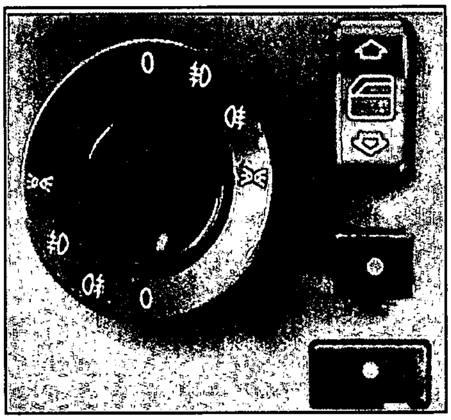

Figure 2-11 Photograph showing the laser mark through material removal mechanism[6].

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[3] Laser Marking Technologies 2002, www.sintecoptronics.com visited in September 2004, Sintec Optronics Pte. Ltd.: Singapore.

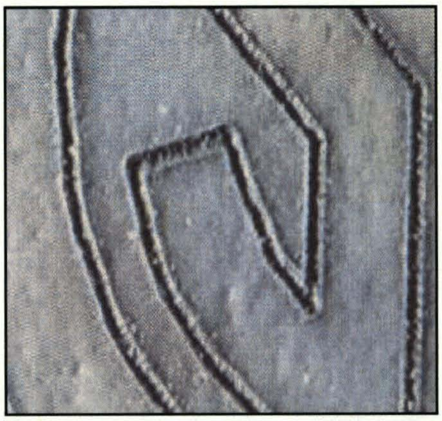
[6] Technical Information on Laser Marking 2001, www.trumpf.com visited in Nov. 2005, TRUMPF Laser Marking Systems AG, Germany.

Foaming

In foaming mechanism the base material melts for a short time during which gases are generated. These gas bubbles occlude into the molten material while cooling, which reflect incident light diffusively and appears to be lighter, as shown in figure 2.11. Unlike other mechanisms, a 'raised' marking is produced in this case[3, 6].

Figure 2-12 Photograph showing the laser mark through foaming mechanism[6].

Engraving



Engraving normally used for marking metals, can be seen only in certain type of plastics. A high power laser is used which partially vaporises the molten material at the surface and produces a groove. The molten material at the surface reacts with oxygen in the atmosphere to form its respective oxide, which due to its colour makes the mark more visible, shown in figure 2.12[3, 6].

Figure 2-13 Photograph showing the laser mark produced by engraving mechanism[6].

2.7 Selection Criteria for Laser Markable Polymers

Plastics are organic materials that are naturally available or synthetically produced by chemically modifying the natural substances or are synthesised from inorganic and organic raw materials. They mostly consist of carbon compounds which join to form macromolecules, as shown in figure 2.13. Based on this molecular structure they are divided in three different groups:

- Thermoplastics
- Thermosets
- Elastomers

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[3] Laser Marking Technologies 2002, www.sintecoptronics.com visited in September 2004, Sintec Optronics Pte. Ltd.: Singapore.

[6] Technical Information on Laser Marking 2001, www.trumpf.com visited in Nov. 2005, TRUMPF Laser Marking Systems AG, Germany.

Thermoplastics have linear or branched macromolecular chains which are intertwined and do not have any cross links, thus defining its strength and thermal behaviour. Hard to flexible at room temperature, the thermoplastics tends to soften, melt and finally decompose with increases in temperature (approximately between 120°C-180°C).

Thermosets have macromolecules which are closely meshed with each other at several cross linkage points making it very hard. Heating them only slightly affects the mechanical properties since the cross linkages do not permit any displacement and finally decomposes without first softening or liquefying.

Elastomers have interconnected macromolecules similar to thermosets, but are wide meshed which gives the extra elasticity compared to the previous types. Once shaped they also cannot be reshaped and decompose without liquefying when subjected to higher temperatures.

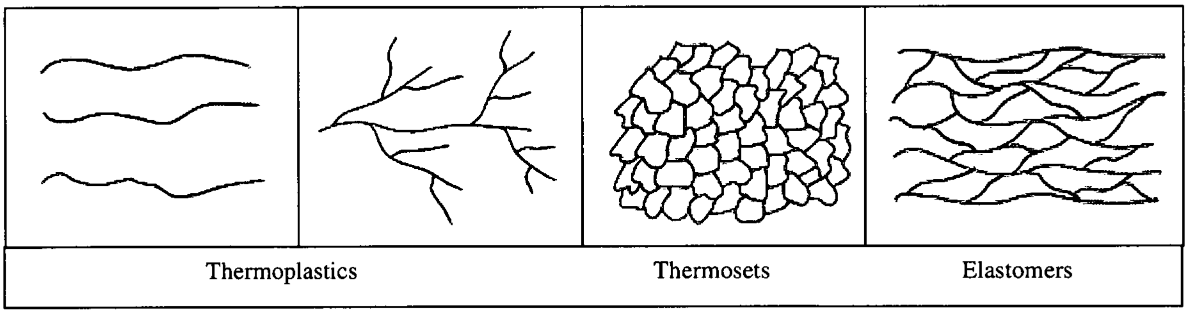

Figure 2-14 showing the macromolecular structures for various types of plastics.

Selection of the appropriate material is the key for success of a product and laser markability is often overlooked in the case of material selection for laser marking applications. Mechanical and Electrical properties are generally considered by product designers/developers to select materials and failure to notice the importance of laser markability of materials during the selection process would result in adverse consequences with unexpected financial implications[7].

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[7] Laser Marking on Plastics Materials, www.rofin-basel.com visited in January 2004, Rofin-Basel, USA.

Therefore, the most important property to be possessed by the laser markable polymers, as the name suggests, is laser markability and this is determined by its ability to absorb a definite laser light wavelength and convert it to thermal energy[8]. Plastics normally absorb light in the UV and far IR range as shown in figure 2.14. Table 2.4 shows the laser markability of various polymers without laser marking additives using CO_2 and Nd:YAG laser at 10640nm and 1064nm respectively. Acrylonitrile Butadiene Styrene (ABS), Polyethylene Terephthalate (PET) and Epoxy resins produce good quality marks compared to the other polymers when marked with an Nd:YAG laser[10]. Even though CO_2 laser produces comparatively good contrast marks, the importance and use of Nd:YAG laser are discussed in earlier sections.

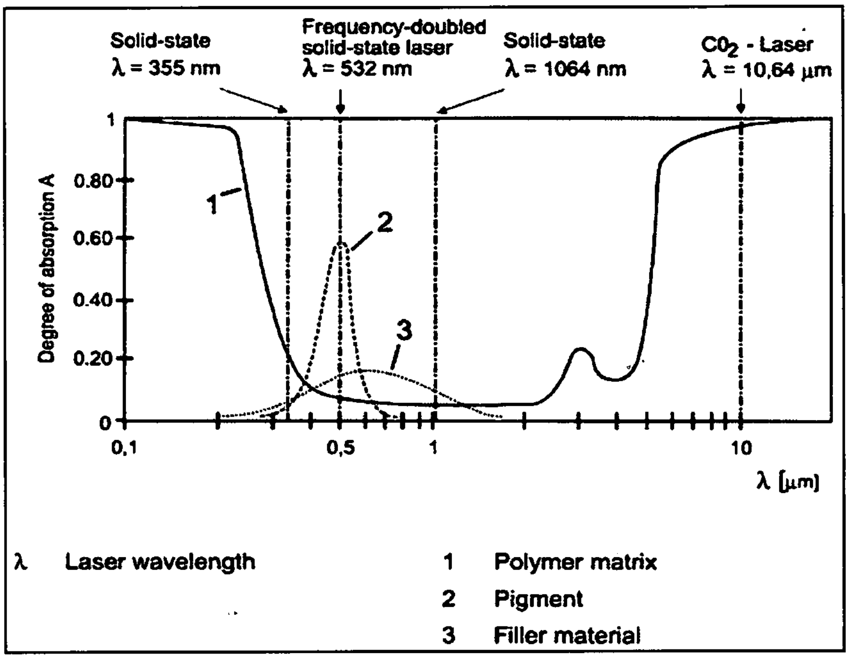

Figure 2-15 Absorption behaviour of plastic and its constituents[6].

With regards to its ability to produce a comparatively good quality laser mark with an Nd:YAG laser, ABS is an ideal choice for manufacturing computer keyboards. ABS also possesses excellent impact resistance and stiffness, hardness and electrical insulation properties. ABS being a comparatively expensive material, it is used in combination with PC to reduce cost of certain computer peripherals with low laser markability requirement. Figure 2.15 shows the

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[6] Technical Information on Laser Marking 2001, www.trumpf.com visited in Nov. 2005, TRUMPF Laser Marking Systems AG, Germany.

[8] Sabreen, S.R., New Technologies of High Speed Colour Laser Marking of Plastics, in Plastics Decorating Mag. 2005, Peterson Publications.

[10] Laser Marking Centre, www.specialchem4polymers.com visited in Jan. 2004, SpecialChem Knowledge and Solution Provider.

molecular structures of ABS and PC, it should also be noted that apart from reducing the costs, PC also imparts good scratch and impact resistance. Like other polymers, absorption properties of ABS at 1064nm are poor and hence additives and fillers are used to formulate a new customized compound which can absorb light at different wave lengths.

TYPE OF POLYMER	QUALITY OF MARKING	
	CO_2 LASER	**Nd:YAG LASER**
Polyethylene (PE)	No Marking	Poor
Polypropylene (PP)	No Marking	Poor
Polystyrene (PS)	Fair	Poor
Polyvinylchloride (PVC)	Very Good	Fair
Acrylonitrile Butadiene Styrene (ABS)	Good	Good
Polyamide (PA)	Poor	Poor
Polyethylene terephthalate (PET)	Good	Good
Polytetra fluoroethylene (PTFE)	Very Poor	Poor
Epoxy	Fair	Good

Table 2.4 Comparison of laser markability of various polymers without any additives[10].

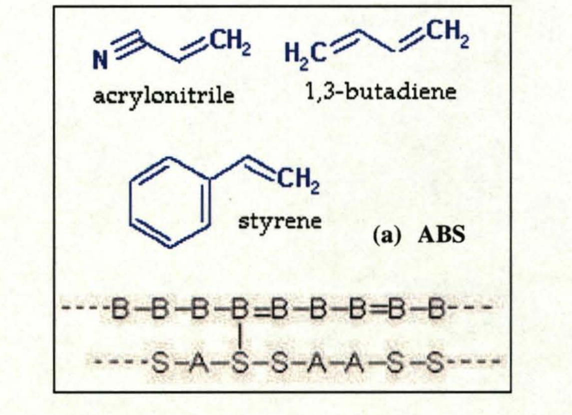

Figure 2-16 Molecular Structure of (a) ABS and (b) PC.

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[10] Laser Marking Centre, www.specialchem4polymers.com visited in Jan. 2004, SpecialChem Knowledge and Solution Provider.

Fig 2.16 shows the strength of some common molecular chemical bonds and laser photon energies, this indicates 1064nm Nd:YAG laser with photon energy of 1.2eV requires many more photons or more energy to interact with the plastic materials. Therefore the most common additives used for laser making formulations are simple metal oxide coated Mica (mineral), salts of Antimony (Sb), Copper (Cu) and other metals[11], Fe_2O_3, TiO_2, Al_2O_3[10] and SiO_2[12] with lower chemical bond strengths. Further, the optical absorption wavelength of a compound which corresponds to the photon energy of a laser, is determined by the band structure and the band gap of the compound[13].

In an atom the bands filled with high energy level electrons (the electron orbit farthest from the nucleus) is referred to as Valence Band and the band outside this is the Conduction Band. This energy width of the forbidden band between the valence band and the conduction band is referred to as 'Band Gap' as shown in figure 2.17. This band gap is like a wall that the electrons must jump over to move freely and the amount of energy to cross the barrier is 'Band Gap

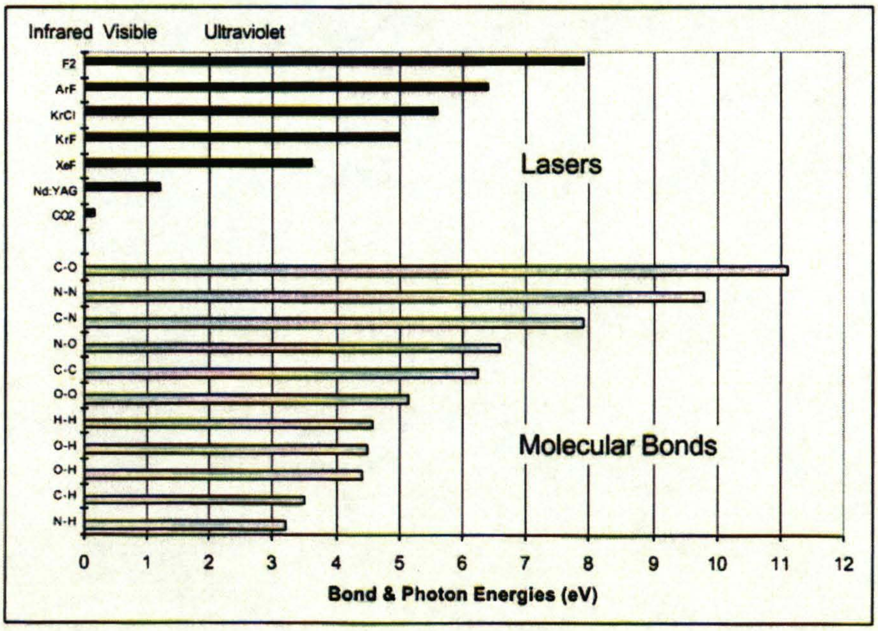

Figure 2-17 Comparison of bond dissociation energies of molecules and laser photon energies[13].

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[11] Graff, G., Laser Marking makes Bigger Imprint in Plastics visited in 2004, www.omnexus.com, Omnexus.

[12] Hoffmann, P., Micro-usinage Laser, STI, Microtechnique, Ecole Polytechnique Federale De Lausanne, France.

[13] Amemiya, S. (2004) Titanium-Oxide Photocatalyst, Three Bond Technical News Issued in January 2004, Three Bond Company Ltd., Japan.

Energy'. This band gap energy principally determines the optical absorption wavelength of the compounds[13]. Table 2.6 shows the compounds used to produce various laser sensitive formulations along with the band gap energy, the additives and the reason for selecting them.

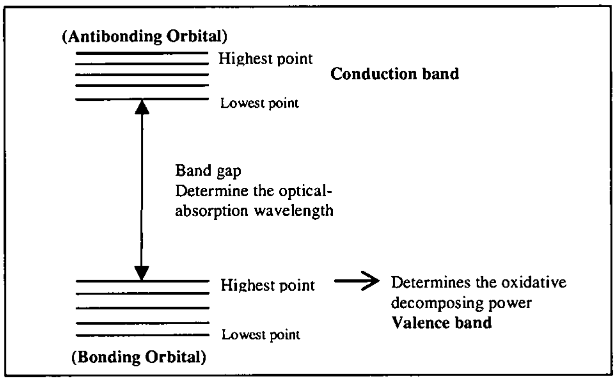

Figure 2-18 showing the band structure[13].

The laser-material interaction is an intricate and complicated process which depends on several factors. Unravelling the minute characteristic phenomenon involved in this process is a part of the work. Apart from the factors already discussed above, which effect the laser-material interaction, size and shape of the additive particle is also an important characteristic. It is understood that spherical particles absorb less energy when compared to the sharp edged particles with a similar surface area. Further, particles with smaller sizes have more surface area for interaction to occur which might absorb more laser energy possibly generating a high contrast laser mark. In the present work, micro and nano sized particles were employed in order to study and understand the above stated phenomenon, for which the results are discussed in chapter 4.

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[13] Amemiya, S. (2004) Titanium-Oxide Photocatalyst, Three Bond Technical News Issued in January 2004, Three Bond Company Ltd., Japan.

Additives	Band Gap Energy	Reason for selecting the additives
Titanium dioxide (TiO_2)	3.0-3.2eV	With absorption wavelengths of 413-386nm, TiO_2 is an active photo catalyst[13, 14].
Aluminium trihydroxide ($Al_2O_3\,3H_2O$)	3.2eV	With absorption wavelengths of 388nm [15] $Al_2O_3\,3H_2O$ + laser (hv) → $Al_2O_3 + 3H_2O\uparrow$ (white compound)
Iron oxide (Fe_2O_3)	2.3eV	With absorption wavelengths of 519nm [16] Low cost materials with efficient marking[10]
Silicon (Si)	1.1eV	With absorption wavelengths of 1100nm, should be ideal for the YAG laser with 1064nm wave length
Mica	--	Generates good marking[10] and certain grades expands 30 times by volume when heated
Azodicarbonamide (AZD)	--	A good blowing agent when heated over 200°C[17]
Bone char	--	Contains mostly Calcium Carbonate $CaCO_3$ + Laser (hv) → CaO (white) + $CO_2\uparrow$
Silver coated glass	--	Silver with absorption wavelength of 328.1nm[17] and glass with the ability to absorb most of the ultra-violet and infrared light were combined to study their affect under the laser.
Nano-additives Nano TiO_2 Nano ZnO Nano CuO	--	With increased surface area of the nano particles, the laser materials interaction or chemistry is thought to be different and the formulation where produced with in house nano-compounds
Merck (Iriodin) & NMB	--	Were formulated to serve as a baseline for comparing with other laser marks

Table 2.5 Different additives selected for formulating laser sensitive materials.

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[10] Laser Marking Centre, www.specialchem4polymers.com visited in Jan. 2004, SpecialChem Knowledge and Solution Provider.

[13] Amemiya, S. (2004) Titanium-Oxide Photocatalyst, Three Bond Technical News Issued in January 2004, Three Bond Company Ltd., Japan.

[14] Zheng, H., Laser-effected Darkening in TPEs with TiO_2 Additives, Singapore Institute of Manufacturing Technology, Singapore. Article available from www.sciencedirect.com, Science Direct, June 2003.

[15] Mustafina, V.N.K.a.N.T., A study of the optical absorption induced in vacuum thermolysis of aluminium trihydroxide Journal of Applied Spectroscopy, May, 1998. **Volume 65**(3): p. 5.

[16] Chun-Liu Fang, K.Q., Jianhua Zhu, Shangbin Wang, Xiaoxuan Lv and Shu-Hong Yu, Monodisperse α-Fe2O3@SiO2@Au core/shell nano-composite spheres: synthesis, characterization and properties. IOP, Electronic Journal (Nano Technology), 2007: p. 7.

[17] Brydson, J.A., Plastic Materials. 4th ed. 1999: Butterworth Scientific publication, page no.119-150.

2.8 Patent Search

There are relatively few referred journal publications where the main focus is laser marking polymers. This is perhaps because developments in this area have almost immediate commercial application. Laser marking of polymers is a challenging research area which is explored within the industry and the results are normally filed as patents, which might be a reason for the lack of published journal papers. A section to critique patents was thought to be fundamental and would also balance for the insufficiency of journal papers.

Citing websites is not a conventional procedure for referencing but on this one instance where the availability of published papers is scarce, using website references was intuitive and unprompted. Further, it should also be noted that not all websites are worth the value but searching websites with required information in PDF format is believed to be more competent and trustworthy. The latter type, are generally research reports or process review documents of the specific company, which were mostly used in the current literature review and barely a few websites material was used in certain cases- only to show figures, photographs or general information.

P1: Additive for YAG Laser Marking

In this patent the author describes a new additive which is designed to impart little or no colour to the plastic and provide a high contrast dark mark when marked with a YAG laser. Previously additives were developed for CO_2 laser marking rather than for 1064nm Nd:YAG laser marking and they also affected the colour of the base material. A calcined powder of co-precipitated mixed oxides of Sn and Sb, where the level of Sb_2O_3 is up to 17% is the additive, which is mixed with the base polymer (Polyethylene (PE), Polypropylene (PP), Polymethyl methacrylate (PMMA), Polybutelene terephthalate (PBT), Polyvinylchloride (PVC)) in the range of 0.05 – 0.1% (by weight) to produce the required dark contrast mark compared to the surroundings[18]. The subject aim of work is to generate light coloured laser marks on dark/black coloured compounds with ABS as the base material.

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[18] James B Carroll Jr. and Steven A Jones, Patent on Additive for YAG Laser Marking 2004 (Patent No. US 6693657 B2), Engelhard Corporation, NJ (USA): USA.

P2: Laser-Markable Plastics

A brief explanation on Laser-Material interaction is given by the author in this patent, absorption of laser beams and hence interaction with the material is dependent on the chemical structure of the plastic and on the laser wave length, therefore use of various additives as absorbers is necessary which makes plastics laser-inscribable.

The additives comprise of a dopant metal/semi metal and pigments, which include a combination of Silicon (Si), Mica flakes, Calcium Chloride ($CaCl_2$), Titanium Dioxide (TiO_2), Iron Oxide (Fe_2O_3) or Tin/Antimony Oxide (Sn/SbO_2). Mixing this additive preferably in the range of 0.3-3% by weight of the base polymer (PE, PP, PBT, PMMA, ABS, Polycarbonate (PC), Polyamide (PA), Polyester etc.) produces a dark coloured abrasion resistant and high contrast inscription on a bright coloured base material when marked under a CO_2 or an Nd:YAG laser[19]. In the present investigation Si, TiO_2 and Fe_2O_3 were alone used as additives and also in combination with ABS as the base material, to generate a light coloured mark. The subject additives have shown reasonable markability when compared to the other additives used and more work is to be carried out to assess the markability characteristics and comment.

P3: Laser Markable Acrylonitrile Butadiene Styrene (ABS) for Telecommunication Terminals/Keypads

ABS exhibits good impact strength even at low temperature, it is stiff, dimensionally stable, relatively easy to machine and can be made with an aesthetic finish. All these factors make ABS the front runner for manufacturing telecommunication terminals/keypads. The patent claims that a laser markable formulation includes 20-24% of Acrylonitrile, 14-17% of Butadiene and 59-63% of Styrene by weight and Carbon black, red Iron Oxide (Fe_2O_3), Titanium Oxide (TiO_2), Silicon Dioxide (SiO_2), Zinc Carbonate ($ZnCO_3$) and Aluminium Hydroxide ($Al(OH)_3$).

Further, it claims that when the above compound is laser marked by a 1064nm Nd:YAG laser generates a dark coloured mark on a bright background with a colour notation, as defined in a 3D colour system of the colour value (L-67.53, a*-1.15 & b*-3.46*) when measured using a Chroma meter. L represents Value which changes from lightness to darkness, a* is Hue and corresponds

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[19] Kniess Helge, Dieter Heinz, Reiner Delp, Gerrard Pfeff and Matthias Kuntf, Patent on Laser-Markable Plastics. 2004 (Patent no. US 6727308 B2), Merck Patent Gesellschaft mit beschrankter Haftung: Germany.

to colour density and b* is Chroma which represents saturation of the colour i.e. from bright vivid to a dull colour in the same shade (referred to as contrast, colour and intensity respectively, for an easy understanding)[20]. Further, it should be noted that discussion in patent 2 is valid in this case and also aluminium trihydroxide was observed to be the best performer among all the additives used for the research. Colour measurements using a Minolta chroma meter indicate that the maximum colour value of L-47.42, a*-4.34 & b*-4.71 was obtained, when generating a light coloured laser mark on a dark coloured ABS compound with $Al_2O_3\ 3H_2O$ as the additive.

P4: Copper Salts for Laser Marking of Thermoplastic Compositions

This patent describes the use of Copper (Cu) salts such as Copper II Phospate/Sulphate/ Hydroxide Phosphate or Copper I Thiocynate along with the following to produce a dark mark on a bright background when marked with a CO_2 laser.

- Inorganic pigments – TiO_2, ZnO, Sb_2O_3, ZnS etc.
- Organic components - Azo, Azomethine etc.
- Polymer soluble dyes – Anthraquinone series etc.
- Possibly typical fatty acids like Stearic acid or Behenic acid etc.

CIE *L*a*b** (CIELAB) is the most complete colour model used conventionally to describe all the colours visible to the human eye. It was developed for this specific purpose by the International Commission on Illumination (*Commission Internationale d'Eclairage*, hence *CIE*). Further, DIN 6174 standard includes 'Colourimetric evaluation of colour differences in surface colours'. Therefore, according to CIELAB method DIN6174, ΔE which is the difference in contrast between the surfaces if ≥ 20 is sufficient for a good contrast mark and in this patent the laser formulation generates a mark with $\Delta E \approx 24\text{-}33$[21].

Further, from the research it is observed that even with values of $\Delta E \geq 20$, the durability performance of the laser marked characters was poor. Laser marked samples which were subjected to the unique durability test regime, which includes the affects of wear caused by

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[20] Jae Hong Choi, Patent on Laser Markable ABS polymer for Telecommunications Terminals and Keypads. 1999 (Patent no. 5981640), Lucent Technologies Inc., NJ (US): USA.

[21] Rein M Faber, Theodorus L Hoeks and Andre Volkers, Patent on Copper Salts for Laser Marking of Thermoplastic Compositions. 1996 (Patent no. 5489639), General Electric Company: Netherlands.

impact, light and sweat, have actually failed the test since the laser mark was completely obliterated in a short length of time, indicating a necessity to spruce up the standards to accommodate the durability performance in the subject case.

P5: Bismuth containing Laser Markable Compositions and Methods of Marking

In this patent, mixing the additive with thermoplastic is carried out in an extruder/ brabender or similar equipment with the formulation $Bi_xM_yO_z$, where M is preferably Zinc (Zn), Silicon (Si), Zirconium (Zr), Aluminium (Al), Tin (Sn) or Iron (Fe) and with x between 2-64, y between 0.3-4 and z between 2-98. The above compounds are formed by high temperature reaction of Bismuth Oxide and other Metal Oxides, which produce a dark coloured mark on light coloured plastics with $\Delta E \geq 20$, 30 or 35 (CIELAB surface colour measurements)[22]. In the current research program, combination of Si and Fe_2O_3 with Al_2O_3 have shown good contrast when compared to some of the least performing laser markable compounds, but more work is required to be carried out to comment.

P6: Laser Markable Plastics

This patent describes the additives which produce a high contrast white mark on dark backgrounds. The additive consists of Graphite powder/flakes coated with Calcium Carbonate ($CaCO_3$) or Calcium Sulphate ($CaSO_4$) or Iron Oxide (Fe_2O_3) or Turbull's blue which is mixed with the plastic in the range of 0.5 - 2 % by weight. Possible additive compositions include:

- Graphite, TiO_2 and $CaCO_3$
- Graphite, TiO_2, SiO_2 and $(Sn, Sb)O_2$
- Graphite, TiO_2 and $CaSO_4$
- Graphite, SnO_2, Carbon Black and TiO_2
- Graphite + TiO_2 and Turbull's blue[23]

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[22] George E Sakoske and Joseph E Sarver, Patent on Bismuth-Containing Laser Markable Compositions and Methods of making and using the same. 2004 (Patent no. US 6680121 B2), Degussa Metals Catalysts Cerdec AG: Frankfurt.

[23] Tammy E Link, Mark J Tellefsen and Shane F Drener, Patent on Laser-Markable Plastics. 2004 (Patent no. 7169471), EMD Chemical Inc.: USA.

P7: Nanometre Antimony Tin Oxide (ATO) particles comprising Laser Marking Additive

This patent explains the use of Nano-ATO as an additive in the laser marking compound which produces a dark mark contrasting the surrounding areas. The additive comprises of Nano-Tin Oxide (main component), some Sb_2O_3 (up to 17%) along with metal (Al, B, Mg, Cu, Sn, Si or Zn)/semi metal powder and preferable Calcium Chloride ($CaCl_2$), which is mixed with the thermoplastic in the range of 0.01-0.1% by weight. The above laser marking formulation when marked with Nd:YAG laser 1064nm produces a high contrast dark mark on a brighter background, further addition of SiO_2 (Nano) improves the contrast of the laser mark[24]. Results from the work also indicate that nano compounds have performed well when compared to the micro compounds, thus corroborating the patent and confirming that increased surface area is a potential factor in the laser-material interaction scenario.

P8: Laser Markable Plastics

This patent explains the marking method for Polyurethanes or Polyester with an Nd:YAG laser. The additive used in this formulation consists of platelet shaped Mica or SiO_2 coated with SnO_2 doped with Sb/ Arsenic (As)/ Bismuth (Bi)/ Copper (Cu). Compounding the base material with the additive in the range of 0.1 – 2% by weight produces a laser mark with 28% reflection on inscribed area and 68% reflection on the matrix where the reflection values are measured using a PSC quick check 300 and a 670 nm reading pen[25].

P9: Resin Composition for White Marking

This patent demonstrates the use of styrenic or acrylic termers as the base polymer and the additives include higher fatty acid (0.01-2 parts by weight), Carbon black (0.005-2 parts) and TiO_2 (0.05–2 parts) to generate a white mark compared to the surroundings with colour measurements according to the CIELAB of L-72[26]. Laser marked ABS compounds formulated with TiO_2 as an additive, in the current research work, certainly performed better when compared with some of the remaining additives but the colour measurements such as L was 42.35 which is much lower than the value quoted in the patent.

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[24] James B Carroll Jr. and Steven A Jones, Patent on Nanometer Size Antimony Tin Oxide (ATO) particles Comprising Laser Marking Additive. 2004 (Patent Application no. EP20040800763), Engelhard Corporation: USA.

[25] Rainer Linzmeier, Burkhand Krietsch and Frank Prissok, Patent on Laser-Markable Plastics. 2003 (Patent no. US6521688 B1), Merck Patent Gesellschaft mit beschrankter Haftung: Germany.

[26] Hiroshi Sagane, Shinichiro Imanishi and Katsuhiko Sumida, Patent on Resin Composition for White Marking. 2002 (Patent no. US66420449 B1), Daicel Chemical Industries Ltd., Osaka: Japan.

3.0 EXPERIMENTAL WORK

This chapter describes the various experiments carried out to study the following:

- Reasons for poor contrast and durability of the characters on printed computer keycaps.
- Effect of laser interaction on different compounds.
- Produce new formulations which could generate light coloured mark with good contrast and durability when marked with a laser.
- Further, a unique test regime which includes the affect of impact, light and sweat has to be designed to test the performance of the new formulations marked with a laser.

3.1 Materials

A range of different additives, listed in Table 3.1, were mixed with Acrylonitrile Butadiene Styrene (ABS) which is the base polymer to produce laser sensitive formulations.

No.	Additive	Colour of Additive	Name of Supplier	Sample Name*
1	Titanium dioxide (TiO_2)	White	From Lab	T
2	Aluminium trihydroxide (Al_2O_3 $3H_2O$)	White	From Lab	A
3	Azodicarbonamide	Yellow	Alfa Aesar	AZ
4	Iron oxide(Fe_2O_3)	Red	From Lab	F
5	Sliver Coated Glass	Grey	Hart Coatings	SG
6	Micafil (Vermiculite)	Dark Grey	Minelco	MV
7	Phlogopite Mica	Grey	Minelco	MP
8	Muscovite Mica	Grey	Minelco	MM
9	Bone Char	Black	RBH Ltd.	B
10	Silicon (Si)		Fisher Scientific	S
11	Nano Titanium dioxide	White	From Lab	NT
12	Nano Zinc oxide	White	From Lab	NZ
13	Nano Copper oxide	Reddish Brown	From Lab	NC
14	Iriodin (Merck's compound)	Black	Merck	IR
15	NMB compound	--	NMB UK Ltd.	NMB

Table 3.1 Additives for making laser sensitive formulations. ** Acronyms used in the later part of the thesis.*

Terluran (GP22) black, trade name for ABS, was supplied by BASF Germany. Generating a light colour laser mark on a dark background is one of the main aims of the work, therefore black coloured ABS grade was procured from the supplier.

3.2 Compounding

All the materials were weighed using a micro balance, shown in figure 3.1. 50g of ABS was mixed with various additives at different percentages by weight. Mixing the components was carried out using a Brabender compounding machine with a maximum mixing limit of 60g, figure 3.2. Table 3.2 shows the times for various stages involved in compounding which include feeding, blending and removal. Temperature ranges maintained to carry out these operations are also included in table 3.2.

Figure 3-1 Sauter Micro Balance.

Parameters	Feeding	Blending	Removing
Time, mins.	10	20	10
Temperature, °C	160	180	160
Revolutions, rpm	3	40	3

Table 3.2 Time and temperatures for compounding samples.

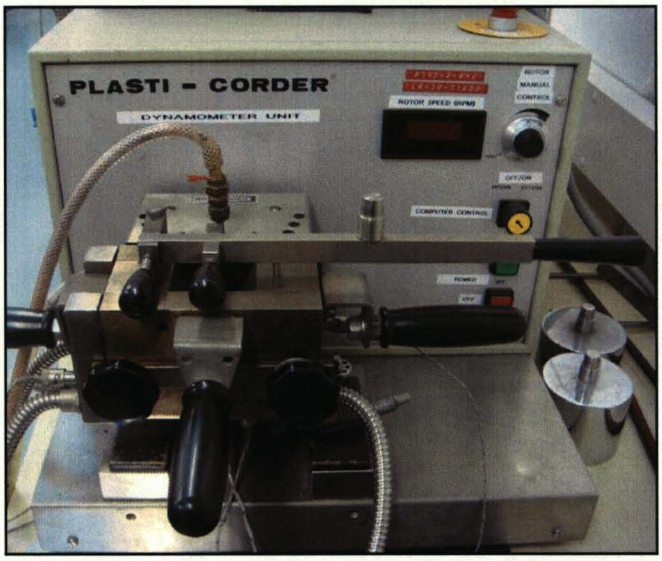

Figure 3-2 Brabender Compounding Machine.

3.3 Compression Moulding

20g of the mixed compound was weighed and pressed under the 2T hydraulic press, shown in figure 3.3, to produce 150x100mm plaques. Top and bottom platens of the press were set to 170°C. Mould plates, shown in figure 3.4, used to hold the sample for pressing were made of mild steel (MS) instead of aluminium to increase plate stiffness and avoid buckling. MS plates improved stability and also prevented the thermoplastics materials adhering to the mould plates. Further, the mould plates are preheated before every plaque is pressed to make the process energy efficient. Table 3.3 shows the heating and cooling cycles involved in the moulding process along with the temperature and pressure settings.

Parameters	**Heating**	**Cooling**
Time, mins.	3	5
Temperature, °C	170	Water cooled
Pressure, MPa	15	10

Table 3.3 Compression moulding times and temperatures.

Figure 3-3 Hydraulic Press for Compression Moulding.

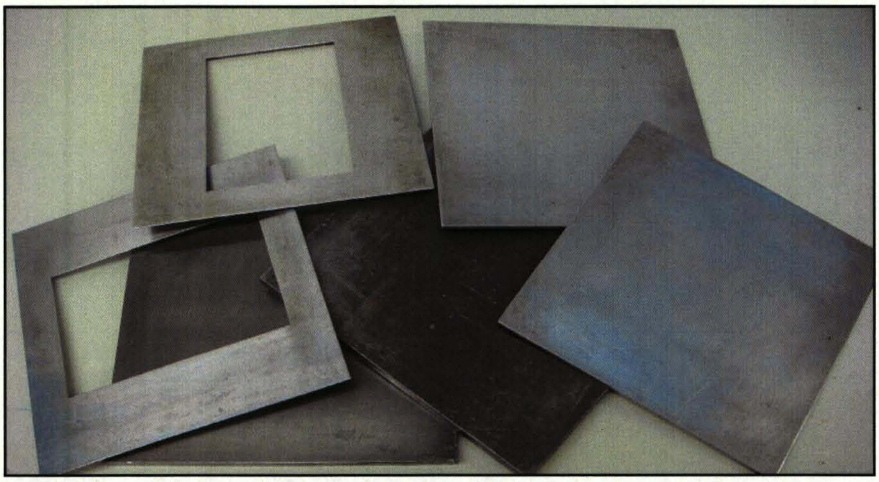

Figure 3-4 Mould Plates used to produce the plaque.

3.4 Laser Marking

As stated in Chapter 2.0 (Literature Search), it is evident that Nd:YAG laser is predominantly used for marking plastics. Initially NMB Minebea (UK) Ltd. agreed to laser mark the samples but the company has moved its operations from Glasgow to Bratislava in Slovakia during the course of the project. A number of alternative options have been tested to laser mark the samples which include;

- Marking the samples at Napier University using a 2321 Nd:YAG laser supplied by LOTUS, since this laser product series has been discontinued and an important power supply component could not be replaced, laser marking the plaques was not possible.
- A number of experiments carried out to study the effect of high power 5V green LEDs on plastics proved to be unsuccessful but the knowledge gained is vital.
- A solid state green laser was used to mark the plastics but unable to control power, speed and frequency of the equipment made this alternative unviable.

Finally, Thinklaser Services and Systems, supplier of laser marking equipment and services based in Surrey, agreed to laser mark the plaques. An Nd:YAG laser, shown in figure 3.5, was used to mark the plaques at different speeds, power and frequency setting.

Figure 3-5 Laser Marking Process.

3.5 Chromometry

Chromometry is the study of measurement of colour (contrast) using a Minolta Chroma Meter model 221, figure 3.6. The Minolta chroma meter, uses a 3mm diameter area to evaluate the colour over a flat surface and represents that colour in the form of three co-ordinates namely L, a*, b* - where L is the Value, which changes from lightness to darkness that moves vertically along the axes of the colour wheel, shown in figure 3.7[27]. a* is Hue, is the colour which makes the colour wheel and b* is the Chroma which is saturation of the colour i.e., from bright vivid to a dull colour in the same shade that changes horizontally. Table 3.4 shows the common representation of the colour co-ordinates. An average of three readings is taken for each sample to determine the difference in contrast of each sample.

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[27] Knowing Colours, Handbook for Minolta Chroma Meter, Published by Minolta, Page no. 1-20.

Colour Co-ordinates	Scientific Name	Common Name
L	Value	Contrast
a*	Hue	Colour
b*	Chroma	Intensity

Table 3.4 Representation of colour co-ordinates.

Figure 3-6 Minolta Chroma Meter.

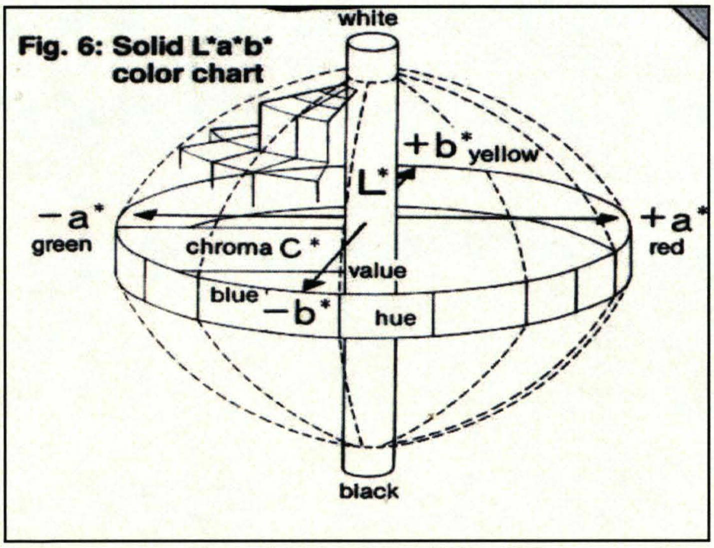

Figure 3-7 The Colour Wheel[27].

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[27] Knowing Colours, Handbook for Minolta Chroma Meter, Published by Minolta, Page no. 1-20.

3.6 Durability Analysis

Determining the durability performance of laser marked keycaps is important and involves wear caused by factors such as impact, light and sweat. The tests are therefore designed to simulate practical working conditions which take account of these factors. The laser marked characters on computer keyboards is important because they can lose their contrast and definition and wear out in relatively short time. Clearly it is the typing process that contributes to the loss of clarity but this involves several factors including impact; degradation mainly due to UV light; and chemicals excreted from the fingers (i.e. sweat). The tests include:

- Specialised Wear Test
- Accelerated Chemical Resistance Test
- Accelerated Ultra Violet Weathering Test

3.6.1 Specialized Wear Test

Wear caused by impact of fingers on keycaps while typing, on those characters used most frequently during typing such as a,e,i,o,u etc., may be of less importance in the initial stage. Over a period of time the wear factor multiplies and finally results in discolouration of the printed character. Specialised wear testing equipment, a scrub testing machine, is used to determine the effect of wear on the printed keycaps. The scrub testing machine, shown in figure 3.8, is set up according to [2] developed at NMB. It is fitted with a wear head made up of a typical polymer resin, which causes wear of the character while testing. The eraser moves horizontally over a

Figure 3-8 Specialised wear testing machine.

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[2] Campbell, A. M., Visual Aids for Keyboard Printing Processes. 2002, NMB Minebea UK Ltd.: Glasgow.

[3] Laser Marking Technologies 2002, www.sintecoptronics.com visited in September 2004, Sintec Optronics Pte. Ltd.: Singapore.

distance of 10mm for 3000 cycles and a load of 450g is applied every time it hits the keycap. After the test, if more than 30-40% of the printed character is worn out as shown in figure 3.9(c) the entire set of keycap samples is rejected or else it is accepted.

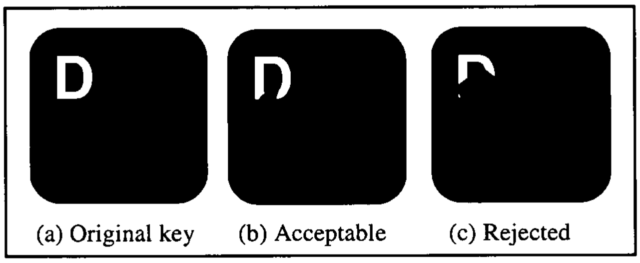
(a) Original key (b) Acceptable (c) Rejected

Figure 3-9 Schematic of the laser marked keycap before and after the wear test.

3.6.2 Accelerated Chemical Resistance Test

Sweat produced from the finger tips also has a gradual effect on the printed characters on keycaps, finally resulting in discolouration. The accelerated chemical resistance test employs two different types of sweat solutions, as described in table 3.5, to study the effect of sweat on keycaps. Samples immersed in the sweat solution are kept in an oven at 70°C for a period of four weeks from which samples are removed at regular intervals and inspected for any changes.

Chemicals	**Acidic (pH-5.5)**	**Alkaline (pH-8.0)**
L-Histidine monohydrochloride monohydrate	0.5g	0.5g
Sodium chloride	5g	5g
Disodium hydrogen orthophosphate dihydrate (or) Disodium hydrogen orthophosphate dodecahydrate	2.2g	2.5g 5g

Table 3.5 Compositions of Acidic and Basic Sweat Solutions.

3.6.3 Accelerated Ultra-Violet Weathering Test

Light from natural and artificial sources affects the contrast of the printed character on the keycap over a period of time. Studies were carried out to determine the amount of discolouration caused by light using a QUV accelerated weathering tester. Figure 3.10 shows the weathering tester fitted with UVA-351 lamps. As the lamp designation indicates the light source emits in the

UV range of 315-400nm with a peak at 351nm[28]. This is recommended by the manufacturer for simulating sunlight, filtered through window glass[28]. During the UV exposure test temperature of the chamber increases to 60°C and accelerates the testing conditions. Samples were kept under the UV light for a period of four weeks which were removed at regular intervals and were examined for difference in contrast. Microscopical studies were also carried out on the samples to record any difference in the structure of the laser mark.

Figure 3-10 QUV Weathering Tester[28].

3.7 Microscopy and Photography

Examining the surface of the laser marked area to understand the laser-material interaction is very important. These surface structural studies would corroborate the results obtained from other tests such as chromometry. A variety of techniques are used to record the laser marked surfaces which include Scanning Electron Microscopy (SEM), Optical Microscopy and Digital Photography.

A Cambridge Instruments Stereoscan S90 SEM, figure 3.11, is used to examine the samples and the results obtained are shown in the following chapter which form a major part of the work. Further, optical microscopy is carried out on Leica Optical Microscope shown in figure 3.12 and macroscopic examination of tampo printed and laser marked samples is successfully carried out

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[28] Operating Manual for QUV Accelerated Weathering Tester, Q Panel Company, Published by Q Panel Company, USA.

on this equipment. Finally, Digital photography was carried out on the samples to show the laser marking outline on the plaque which gives a clear indication of the marking pattern. Photographs of samples were also taken to show the effects of wear testing on the laser marked characters.

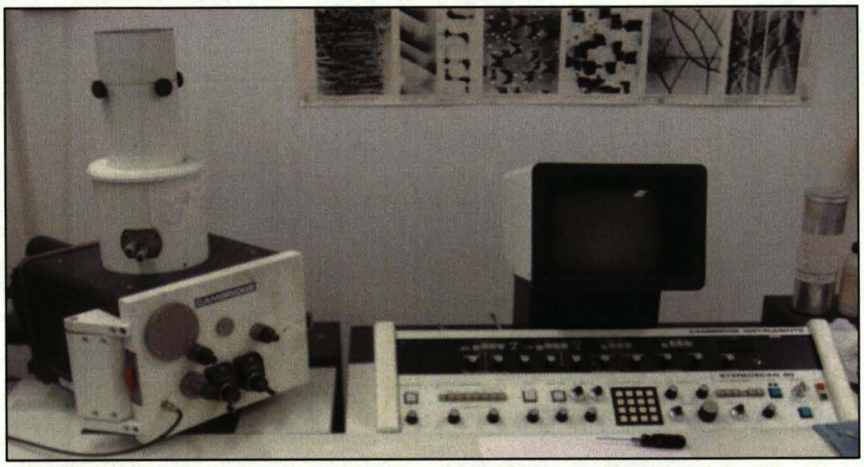


Figure 3-11 Stereoscan S90 Scanning Electron Microscope.

Figure 3-12 Leica Optical Microscope.

4.0 RESULTS AND DISCUSSION

4.1 Tests on Existing Keyboards

Understanding the reasons for lack of initial contrast along with subsequent discolouration of the laser marked, dark coloured samples is one of the main aims of the work. A range of different light and dark coloured keyboards marked tampographically or using a laser were supplied by NMB Minebea (UK) Ltd. Inchinnan to carry out the work. The samples are detailed in table 4.1 shown below, along with the nomenclature.

Sample No:	Keyboard Colour	Type of Printing	Brand name	Sample Name
1	Grey	Tampographic	Dell	GTD
2	Black	Tampographic	Logitech	BTL
3	Black	Tampographic	Laptop	BTP
4	Black	Tampographic	IBM	BTI
5	Beige	Laser	Bell	BeLB
6	Beige	Laser	Logitech	BeLL
7	Black	Laser	Dell	BLD
8	Black	Laser	NMB	BLN

Table 4.1 Nomenclature of the keyboards used for preliminary testing.

4.1.1 Durability Analysis

Printed keycap samples were subjected to a series of durability tests such as specialised wear test, accelerated chemical resistance test and accelerated UV weathering test, in order to estimate the affects of wear caused by impact, sweat and light.

Specialised Wear Testing

Results from the specialised wear test carried out at NMB Minebea (UK) ltd. show less than 10% wear of the character indicating that all the samples passed the test. Nevertheless, the same keycaps exhibit discolouration in actual service conditions, in a period of less than 6 months. Optical microscopy is carried out on the test samples, shown in figure 4.1, to record the loss in character after the wear test.

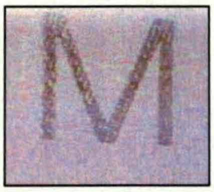
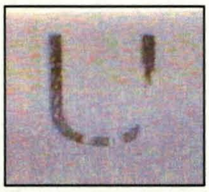
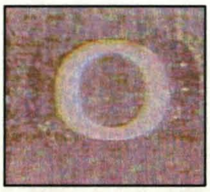
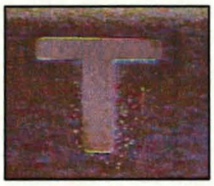
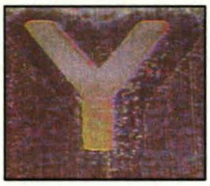
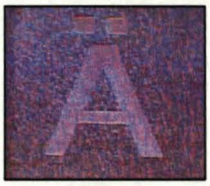
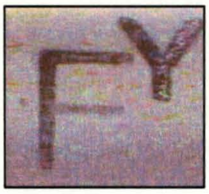
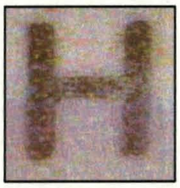
BEFORE TEST	AFTER TEST	BEFORE TEST	AFTER TEST
			
Grey Tampographic Dell (GTD)		Black Tampographic Logitech (BTL)	
			
Black Tampographic Laptop (BTP)		Black Tampographic IBM (BTI)	
			
Beige Laser Bell (BeLB)		Black Laser Dell (BLD)	
			
Beige Laser Logitech (BeLL)		Black Laser NMB (BLN)	

Figure 4-1 Images of specialised wear tested samples with less than 10% wear.

Accelerated Chemical Resistance Test

The custom designed chemical resistance test which estimates the affect of sweat on printed keycap characters was carried out, as described in section 3.6.2, on the supplied samples. Chromometry was also carried out on the test samples after every week to record the change in contrast (colour) using the Minolta chroma meter.

Results show no significant correlation and the microscopic difference seen on the test samples was difficult to capture with the then available optical microscopy equipment in the laboratory. The reasons for insignificant relationships in the results might be due to the Minolta chroma meter considering an area of 3mm diameter on a truly flat surface to measure colour, whereas the keycaps are slightly curved for better ergonomics and the underlying dark/light coloured background is also taken into consideration to measure the contrast of the printed character. Therefore, interpretation of the data from these tests proved difficult.

Accelerated UV Weathering Test

Test samples were kept under UVA-351 lamps for a total period of 6 weeks and measured for any change in the contrast using the Minolta chroma meter after each week. Results from this test indicate a gradual wear in the colour of keycaps with some minor discrepancies. Nonetheless, interpretation of the data is also complicated due to the reasons stated above.

Figure 4.2 and 4.3 show the variation in contrast (Value, L) due to the affect of UV light over a period of 6 weeks and the relevant digital photographs of tampo printed and laser marked keycaps respectively. The line of best fit for a given set of data can be a straight line or a curve depends on various parameters. In this scenario where the colour values (L) are widely spread, linear trendlines are best fit in order to estimate the rate of change in colour (deterioration) with time. Increase in L indicates that the contrast of keycaps is changing from light to dark shades and this is corroborated by the photographs, shown in the figure, over the six week period.

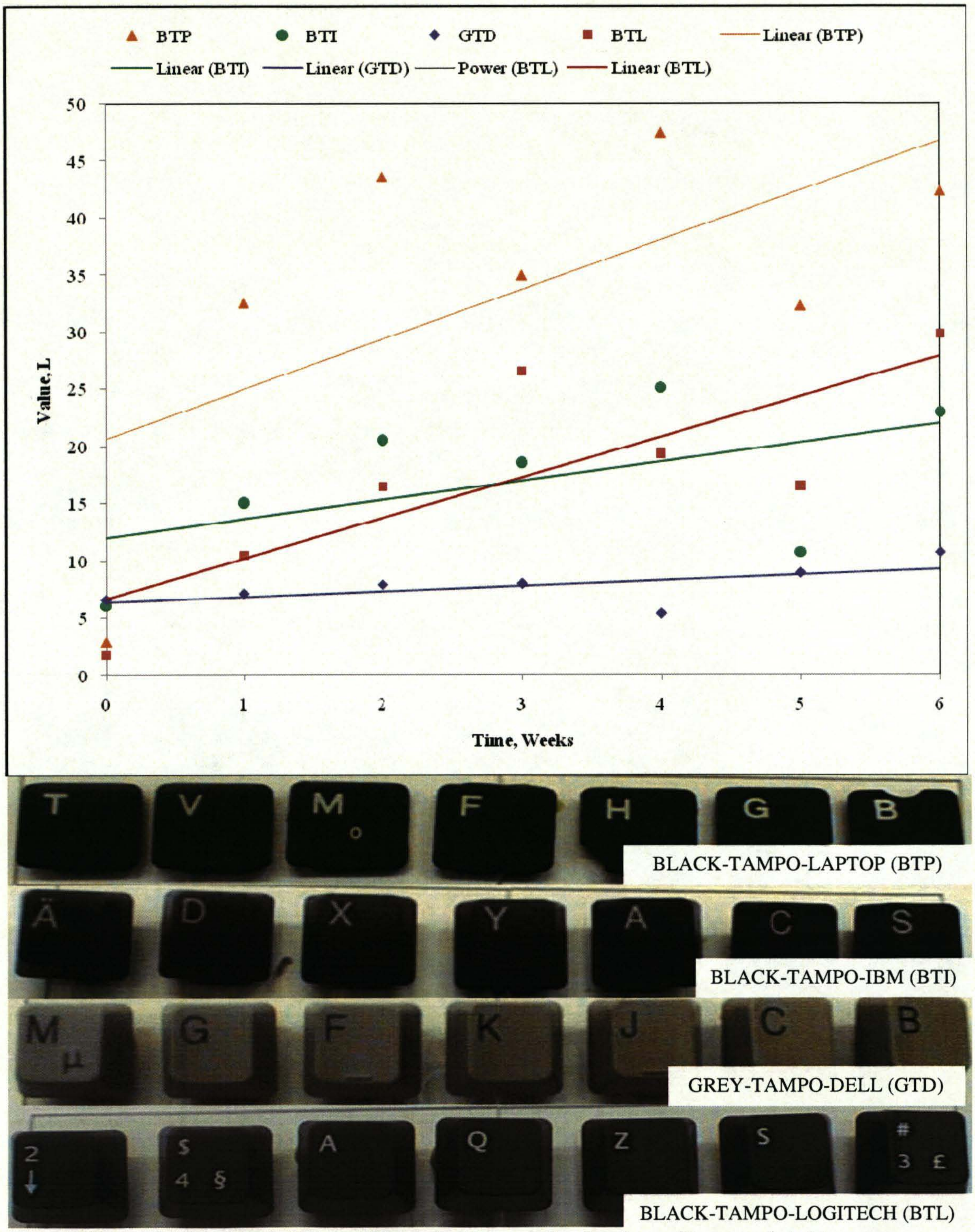


Figure 4-2 Graph and photograph showing the variation in colour of tampo printed keycaps under the accelerated UV weathering tester.

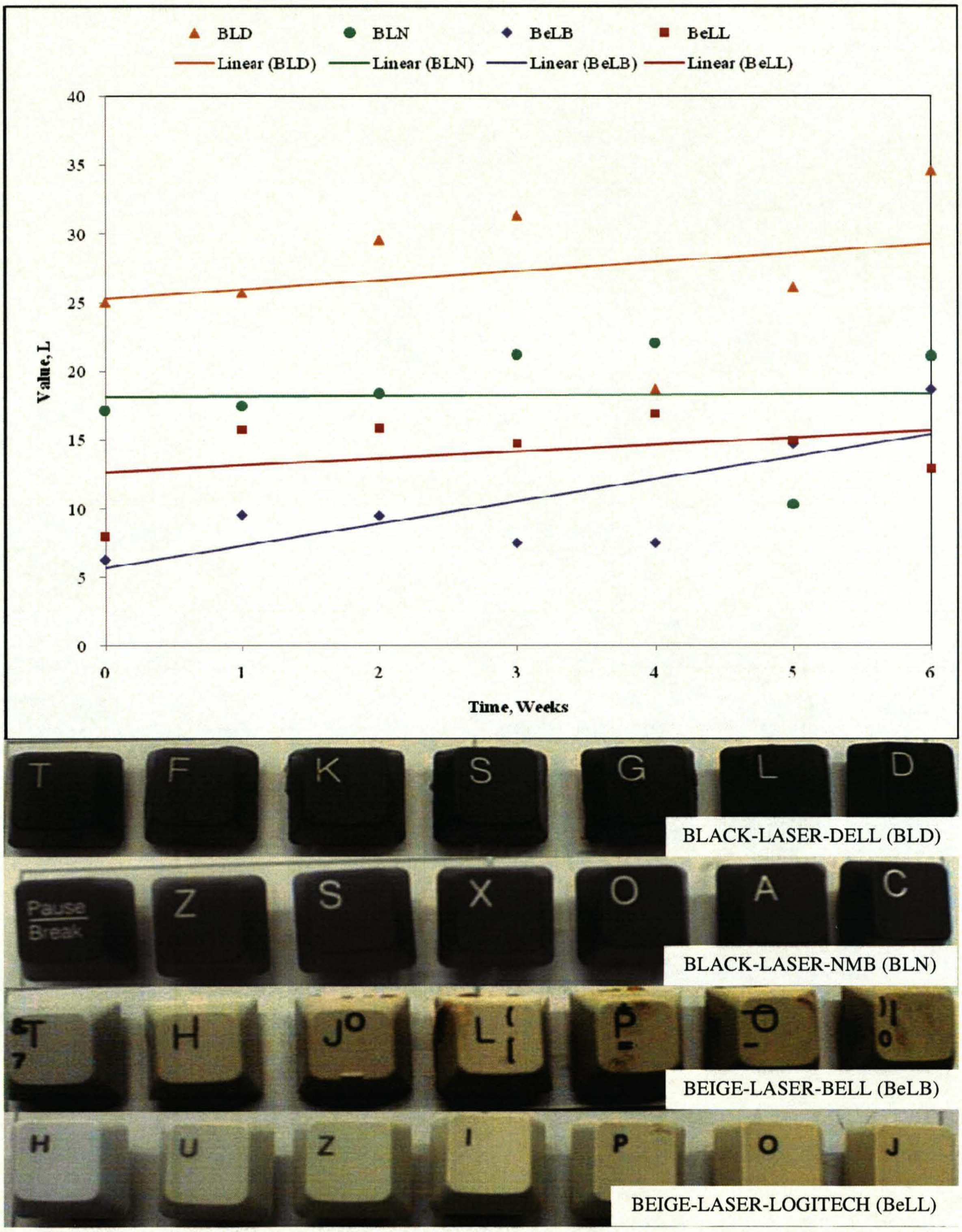


Figure 4-3 Graph and photograph showing the variation in colour of laser marked keycaps under the accelerated UV weathering tester.

4.1.2 Scanning Electron Microscopy

Scanning Electron Microscopy of the laser marked beige/light keycaps show a clear pattern, but no clear outline is visible in the case of tampo printed keycaps. Figure 4.4 a & b show the print pattern on beige coloured laser marked keycaps (BeLB & BeLL). From the micrographs it is evident that both the marks are generated by foaming mechanism, but the texture is entirely different.

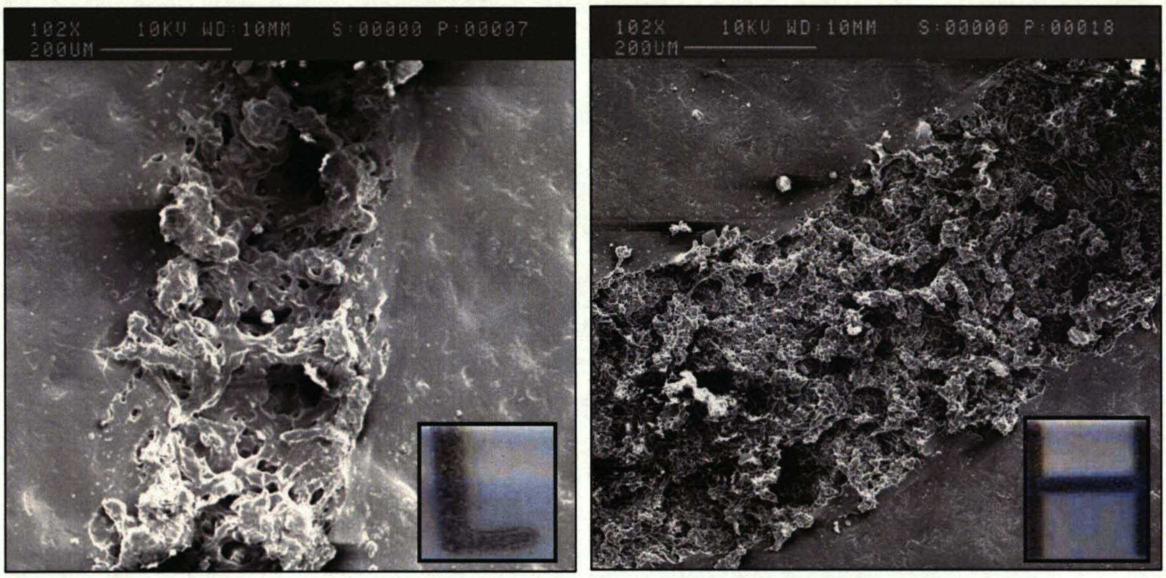


Figure 4-4 a & b Micrographs showing dark colour laser marks on beige coloured keycaps (BeLB & BeLL).

Figure 4.4a depicts a less dense, coarse foam pattern which appears to be shallow and hence in practice this results in a print character with low contrast as shown in the inset photograph. Figure 4.4b shows a dense and fine foam structure which appears to be "raised" thus reflecting incident light diffusively, to make the print character more visible, as seen in the inset photograph. Even though the keycap in figure 4.4b shows better contrast than the keycap in figure 4.4a, discolouration of the printed characters on the keycaps is observed in both the cases within less than 3-6 months in actual application. The foamed material is very brittle and is worn away relatively quickly by typing. This finally might have resulted in wear of the keycaps and reduced the life time expectancy of the keyboards.

BeLB – Beige Colour keycap, Laser marked for Bell
BeLL – Beige Colour keycap, Laser marked for Logitech

Scanning electron micrographs of two different dark/black coloured laser marked keycaps are shown in figure 4.5 a & b (BLD & BLN). It can be seen that both the micrographs reveal the formation of a 'raised' surface – a characteristic of foaming mechanism, with a perfectly plain surface at the top instead of a cellular structure.

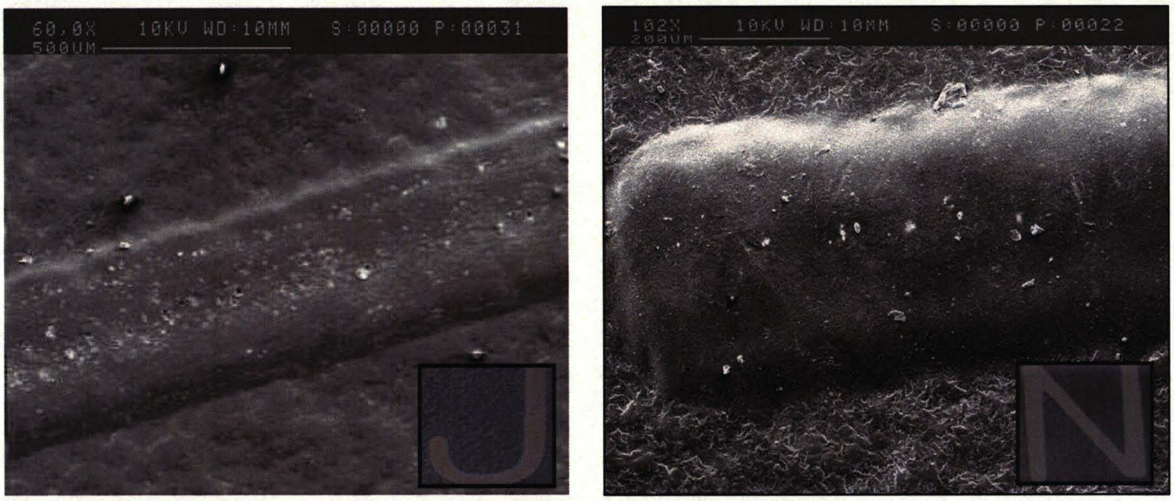


Figure 4-5 a & b Micrographs showing light colour laser mark on black coloured keycaps (BLD & BLN).

Absence of a cellular structure at the surface, which reflects the incident light to make the mark more visible, might be one of the reasons for lack of initial contrast of a light coloured laser mark against the underlying dark coloured keycap. Furthermore, the 'raised' surface tends to 'smoothen' because of the difference in height between the laser mark and the underlying surface which tends to wear down quickly by material loss, due to the abrasive action of the fingers on the keycaps while typing. This results in discolouration of the printed character and a reduced service life for the keyboards.

Understanding the drawbacks associated with laser induced foaming process, the possible marking method which generates good contrast and durability is 'Colour Change' mechanism. In this mechanism, the laser assists in the transformation of the additive in the base material, rather than producing raised foam which is brittle. Consequently the laser marked character is more durable and the keyboard has a longer service life.

BLD – Black Colour keycap, Laser marked for Dell
BLN – Black Colour keycap, Laser marked for NMB

Optical Microscopy

Optical microscopy of the laser marked and the tampo printed samples is carried out using a LEITZ ARISTOMET optical microscope. The tampo printed keycaps show a difference in the surface texture between the base and the UV coated area of the keycap, figure 4.6. The surface texture in the UV coated region is bigger or coarser when compared to the base, this might be due to UV curing which is carried out at 35-40°C, in order to flash off the thinners. Further, the laser marked samples show a plain character with not much variation or detail.

Figure 4-6 Difference in grain size on a black tampo printed keycap.

4.1.3 EDXA Analysis

Analysis of a used and worn out tampo printed keycap, procured from NMB Minebea (UK) Ltd., was carried out using a low power microscope, figure 4.7. Samples were also subjected to Energy Dispersive X-ray Analysis (EDXA) to determine the chemical elements in different areas. Figure 4.7 shows a tampo printed keycap and EDXA analysis is carried out at different areas including the worn out area, UV coated area and also at their interface. The EDXA spectrum show peaks of silver (Ag) since it is the target for sputter coating and this should be discounted. Examination of the EDXA spectra shows presence of silicon (Si) in the worn out area followed by an increase at the interface and even higher amounts of silicon in the UV coated area, shown in figure 4.8.

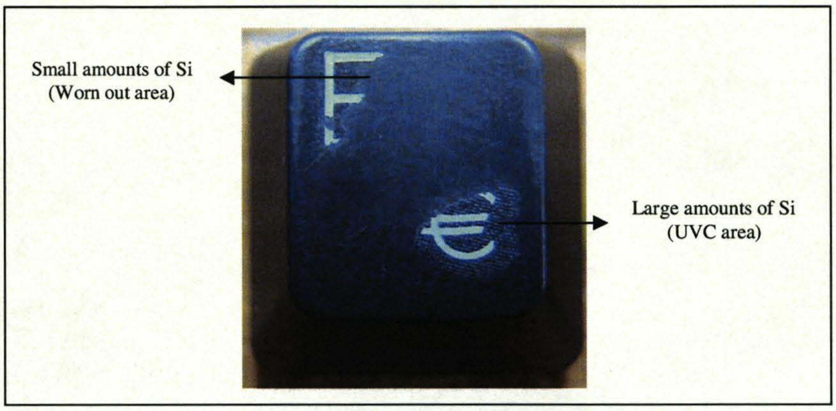


Figure 4-7 Tampo printed keycap showing the worn character.

Certain types of UV curable coatings contain silicon e.g. UV curable silicones, silicone acrylates etc. [29]. The presence of significant amounts of silicon may thus be related to the formulation of UV curable resin. Tests on unused tampo printed keycaps protected by UV curable coatings also show the presence of silicon. Therefore, it is likely that the UV coated area on the keycap being investigated is also protected by a silicone-based coating. Technical data sheets from Thermo-clad which describe UV cured materials[30] suggest that the coating can be 'cleaned up' using acetone and certain acetates, which are also constituents of certain cosmetic chemicals

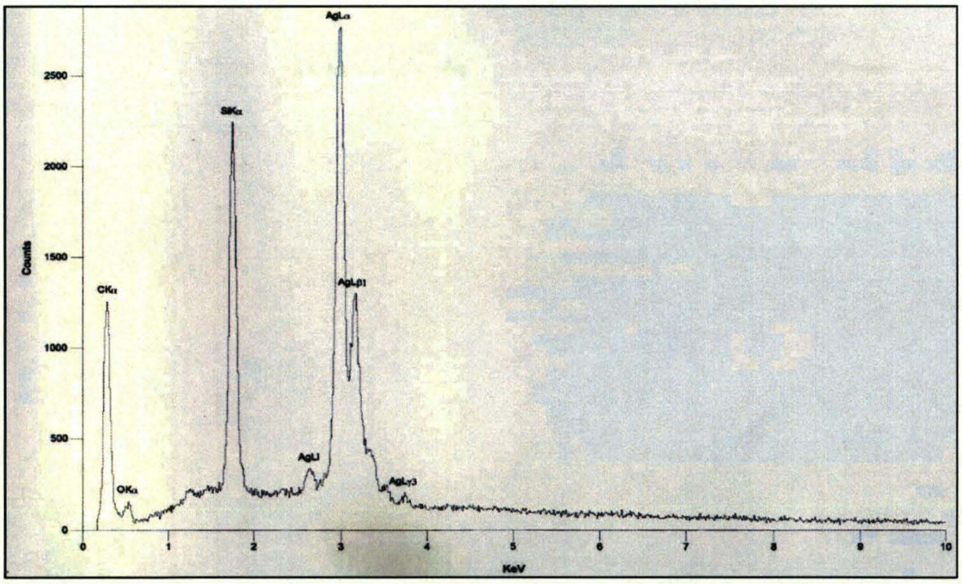


Figure 4-8 EDXA spectrum of the worn out tampo printed keycap.

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[29] Oestreich, D.S., UV Curable Silicones available from 2001, Published by Degussa AG Goldshmidt Industrial Specialities, Germany.

[30] UVPL-4019, D., Clear UV Cure Coating Technical Data Sheet, www.thermoclad.com, Published by Thermoclad, USA,

such as nail varnish etc. Premature removal of the UV coating and underlying printed character might be a result of the user employing, for example, nail varnish or nail varnish remover etc. However, other chemicals containing acetates, ketones etc. cannot be discounted as the keyboard may come into contact with, for example cleaning fluids, hand-creams, lotions etc.

4.1.4 Drawbacks and Recommendations

Commercially available keycaps have passed the specialised wear test, but discolouration of the same keycaps is observed within less than 6 months in service. Steps should be taken to increase the testing time which would help estimate the service life expectancy of printed characters on keycaps. The ergonomics of a keyboard gives a slight curvature to the keycap which is causing problems to measure the contrast (colour) with a Minolta chroma meter since it is built to take measurements from a flat surface. Further, the chroma meter considers an area of 3mm diameter on the flat surface to measure the colour co-ordinates. Therefore, to overcome the above problems a new test plaque has been designed for laboratory testing purposes only and laser marking 5x5mm squares on the flat surface, as shown in figure 4.9, will allow precise measurement of the colour.

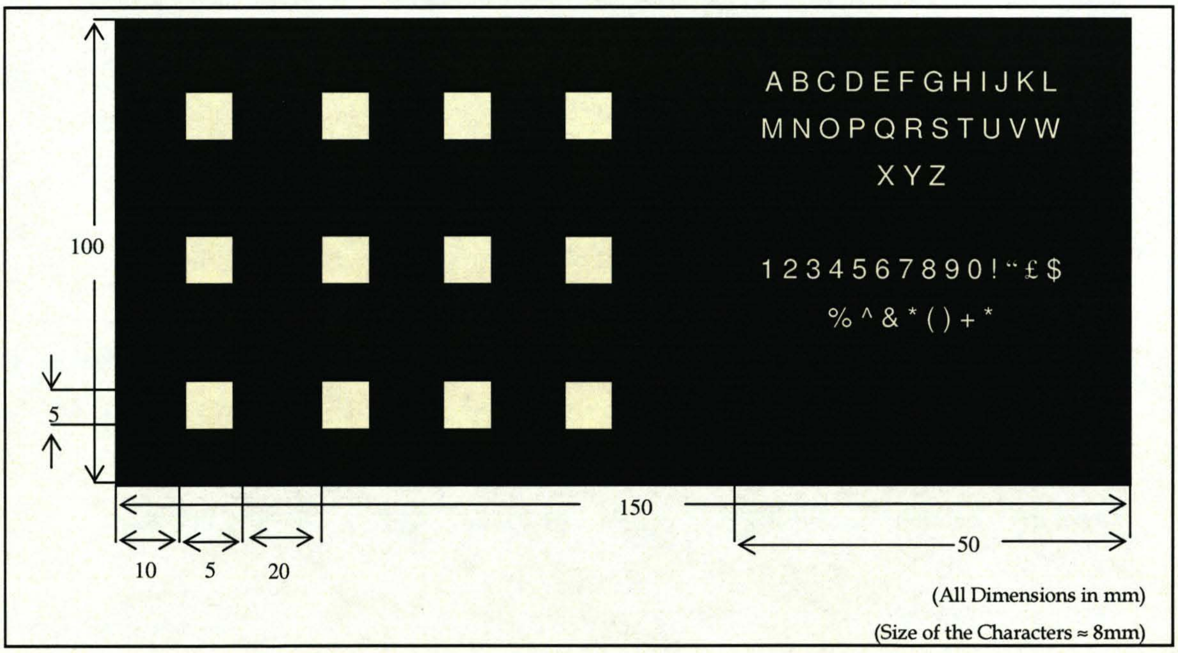


Figure 4-9 Schematic diagram showing the design of laser marks on future test plaques.

Unique Durability Test Regime

Laser marked samples were subjected to a rigorous test regime exclusively designed to estimate the durability of printed characters on the plaques by simulating practical conditions and hence referred as the 'unique durability test regime'. In typical operating conditions wear of the keycap is because of a combination of impact, sweat and light. The outcome is different if the effect of each factor is tested individually. Therefore, samples are kept under the UV light for 16 hours and immersed in sweat solution for 8 hours a day for a period of 4 weeks. The samples are also wiped under the specialized wear testing equipment for 10 minutes every week. Each keycap has been exposed to the wear tester for a total of 40 minutes at the end of the 4 week period. This combines the effect of light, sweat and impact making the test procedure closer to working environment. One sample is removed after every 1 week for chromometry and later subjected to microscopy and photography.

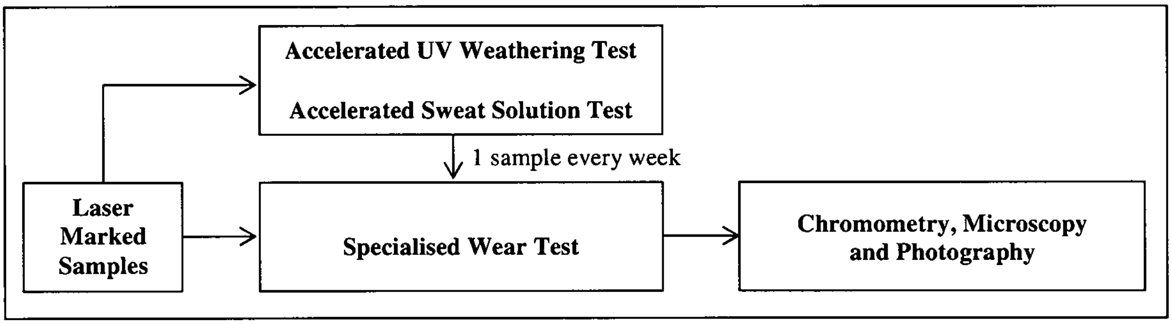


Figure 4-10 Block diagram showing the durability test regime

4.2 Formulations: Batch I

Figure 4.11 shows the overview of an experimental cycle of the work to be carried out. Acrylonitrile Butadiene Styrene (ABS), the base material, was blended with a variety of different additives according to weight percentages as shown in table 4.2. Brabender compounding machine was used for producing the formulations which were then compression moulded to make 150x100mm plaques. Plaques produced were then laser marked with Nd:YAG laser (wavelength 1064nm), good for marking keyboards (plastics). Further the samples were also subjected to the custom designed unique test regime which combines the effects of impact, sweat and light to assist with the development of novel plastics formulation which, when marked with a laser, produce characters with improved contrast and durability. An outline of the selection process of the various compounds is also shown in figure 4.11 which indicates the progress of work at different stages or batches.

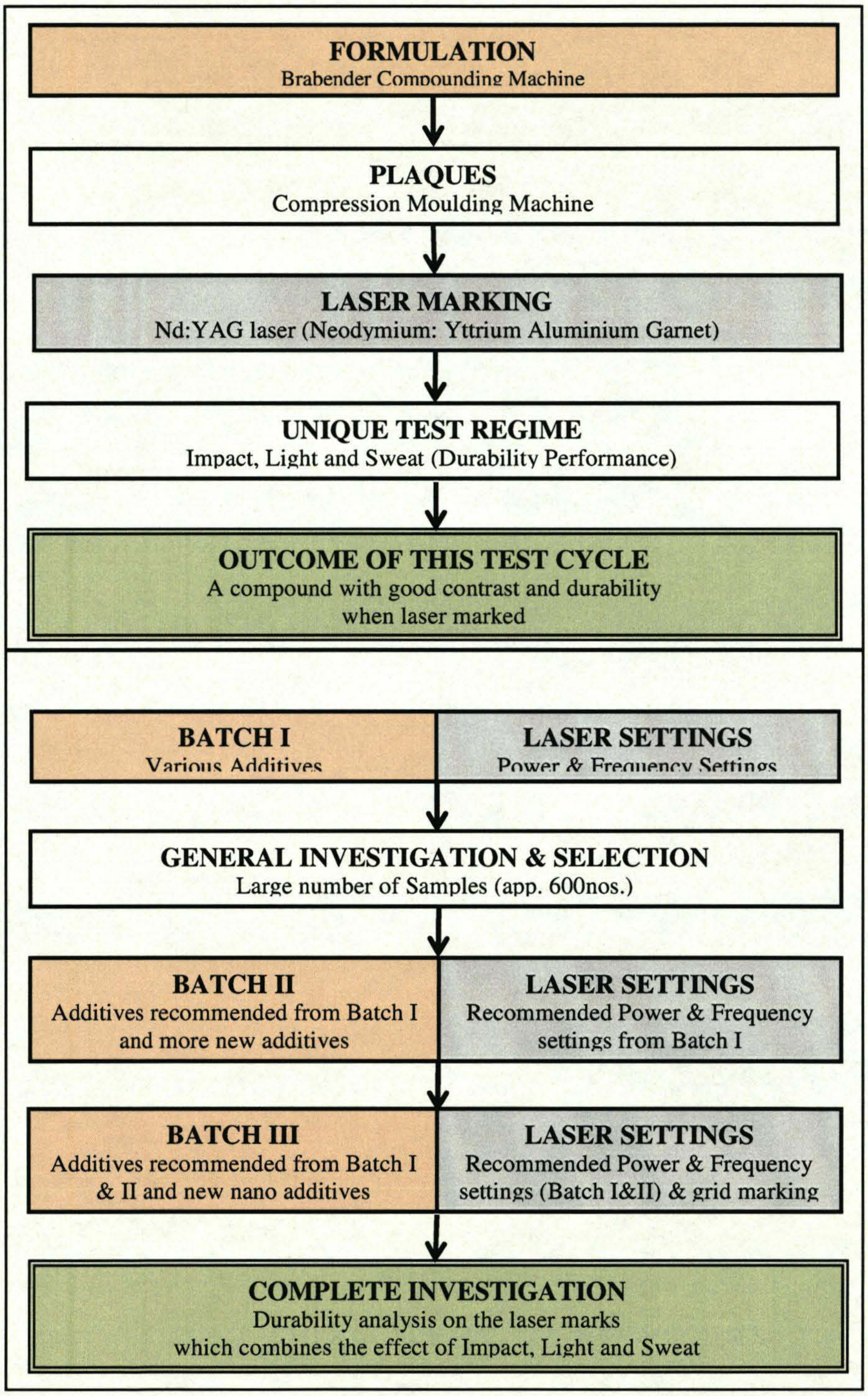


Figure 4-11 Overview of the experimental cycle and selection process.

Sl. No.	Additive	% Additive / Sample Name				
		0.2	0.4	0.6	0.8	1.0
1	Titanium dioxide (TiO_2)	T1	T2	T3	T4	T5
2	Aluminium trihydroxide (Al_2O_3 $3H_2O$)	A1	A2	A3	A4	A5
3	Azodicarbonamide	AZ1	AZ2	AZ3	AZ4	AZ5
4	Iron oxide (Fe_2O_3)	F1	F2	F3	F4	F5
5	Sliver Coated Glass	SG1	SG2	SG3	SG4	SG5
6	Micafil (Vermiculite)	MV1	MV2	MV3	MV4	MV5
7	Phlogopite Mica	MP1	MP2	MP3	MP4	MP5
8	Muscovite Mica	MM1	MM2	MM3	MM4	MM5
9	Iriodin (Merck's compound)	IR1	IR2	IR3	IR4	IR5
10	NMB compound	NMB1	NMB2	NMB3	NMB4	NMB5

Table 4.2 Additives and sample code names used for Batch I formulations.

4.2.1 Problems and Solutions

A number of problems were encountered while working. Initially, the computer-machine interface of the Brabender compounding machine malfunctioned, which resulted in the use of the machine manually rather than in the automatic mode. It took close and critical examination to resolve the problem with the help of the supplier to run the machine automatically. However, operating the compounding machine manually did not show any deleterious effects on the formulation or the procedure, but operating the machine automatically would measure torque and estimates the viscosity or mould flow characteristics of the mix.

The compound adhered to the rotor shafts while blending and removal of the compound took a long time and posed a large problem. A cleaning cycle had to be introduced in between every blending cycle, which increased the processing time reducing productivity. Use of calcium stearate as a lubricant and decreasing the blending temperature from 240°C to 180°C resolved this problem.

Adherence of the blend to the mould plates posed another problem. Use of silicone or non-silicone based mould release agents did not resolve the situation. Plates cleaned with solvents such as Toulene or Methyl Ethyl Ketone (MEK) made the situation even worse which generated white striations on the mould plates, these were then transferred to the plaques reducing quality of the plaques. However, use of PTFE mould release agent solved the problem temporarily. Finally replacement of the aluminium mould plates with mild steel, with better mechanical properties, helped easy removal of the plaque from the mould plates and also solved the problem of aluminium plates buckling during moulding.

NMB Minebea (UK) Ltd. agreed to laser mark the samples but the company has since moved its operations from Glasgow to Bratislava in Slovakia. This has resulted in a limited number of options to laser mark the samples locally. Consultation with Professor Janos Hajto assisted in organising a 5V LED set up to be used for marking the plaques. Even though the LED marking idea is innovative but the total power produced from the setup was insufficient and ineffective on the plastic and the effort proved to be futile. Trials with using a continuous green solid state laser for marking the plaques proved to be unsuccessful due its inability to control any settings such as power, frequency, speed, spot size etc. Finally, Thinklaser Systems and Services, a specialist laser marking, distributing and servicing company in Surrey agreed to laser mark the samples.

4.2.2 Laser Marking Batch I Formulations

The batch I formulation samples were laser marked using a 65W lamp pumped Nd:YAG laser operating at 1064nm wavelength. Marking is carried out at two different scenarios. Initially at a constant pulse rate of 18MHz (Sample code name: A) with increments in power by a factor of 5 from 30% to 50% (Sample code name: 1-5). Further, marking was also carried out at constant power of 35% (B) with increments in pulse rate or frequency by a factor of 5 from 15MHz to 35MHz (1-5), as shown in Figure 4.12. The speed of marking, dot size and dot overlap percentage are kept constant at 1000mms^{-1}, 0.08mm and 30% respectively. The laser marks produced are straight lines rather than 5x5mm squares because these initial formulations are to study laser sensitivity of the additives by examining the SEM micrographs and understand the laser-material interaction and the marking mechanism.

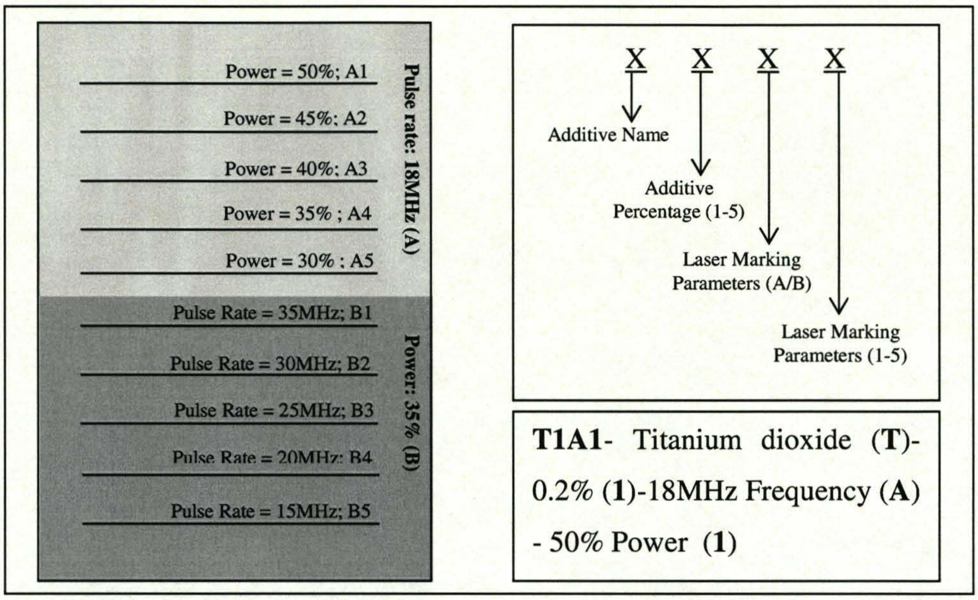


Figure 4-12 Plaque showing the outline of laser marks at different settings and the sample naming procedure for batch I formulations.

4.2.3 X-ray Mapping

X-ray mapping is carried out on a Cambridge Stereoscan S90 model SEM to investigate for any discrepancies in additive distribution and dispersion. Results indicate no clustering of additives and uniform distribution throughout the bulk material as shown in figure 4.13.

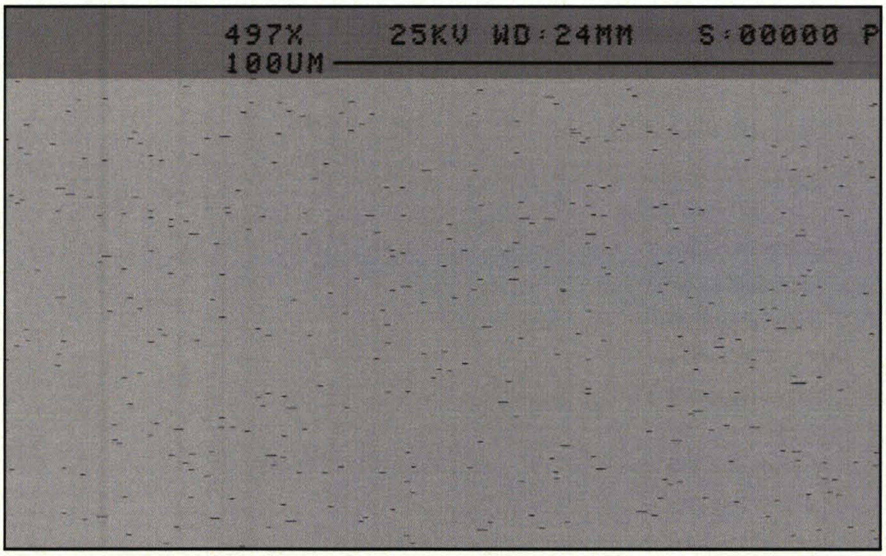


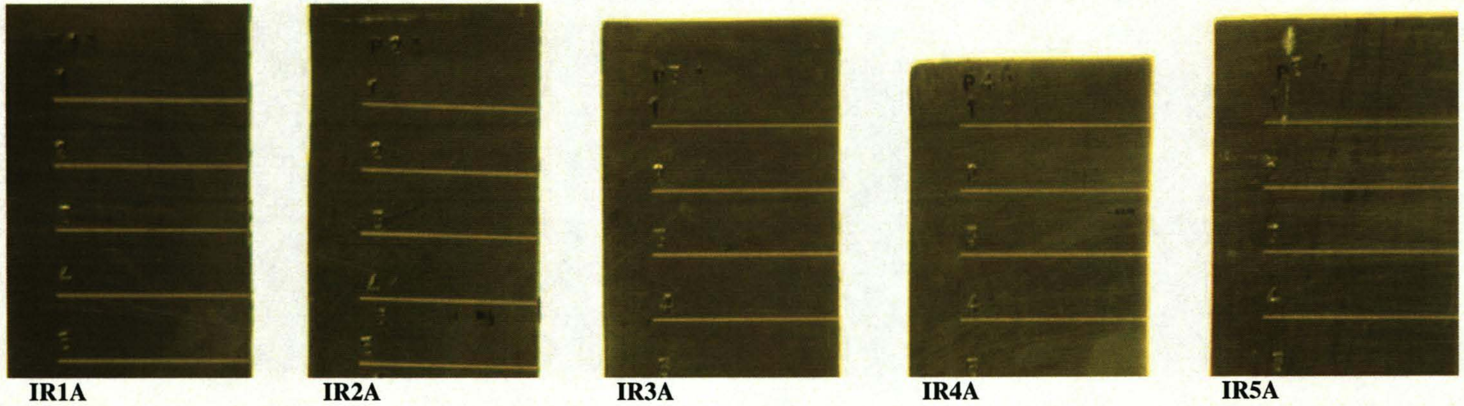
Figure 4-13 X-ray mapping micrograph showing uniform dispersion and distribution of additive in T5A1sample.

T5A1: 1.0% TiO2, 18MHz Frequency, 50% Power

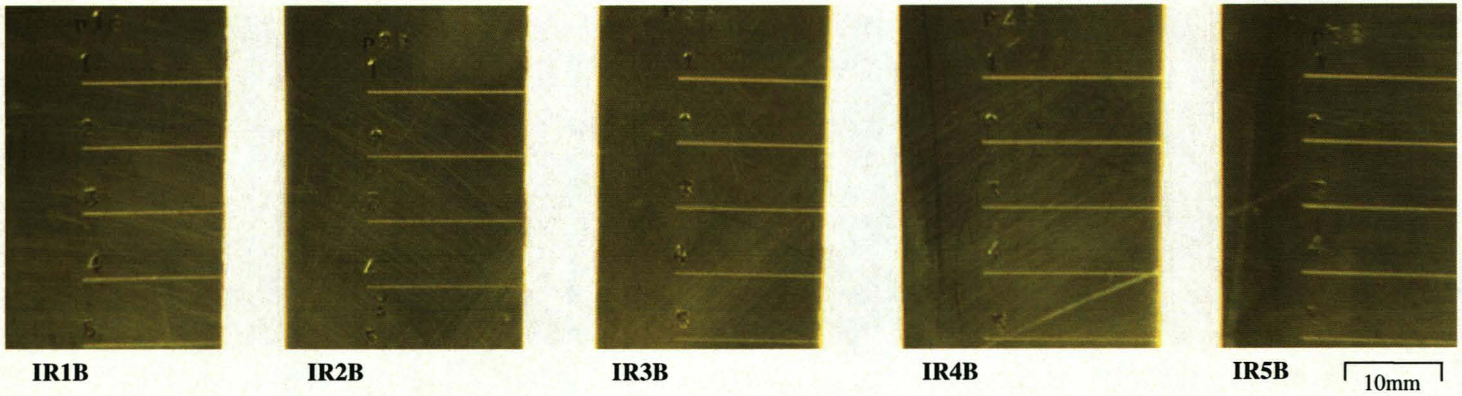
4.2.4 Microscopic Analysis of Batch I Formulations

Laser marks with the additives other than Merck and NMB resulted in poor contrast. Additives including titanium dioxide, aluminium trihydroxide, iron oxide and silver coated glass have shown improved or higher contrast laser marks when compared to compounds with azodicarbonamide, micafil, phlogopite mica and muscovite mica as additives. However, the batch I formulations were prepared in order to investigate the laser sensitivity of the additives. Consequently there was no need to subject these samples to the durability test regime described in section 3.6. Samples blended with Iriodin, Merck's laser sensitive compound, marked with the laser at different power and frequency settings are photographed digitally and shown in Figure 4.14. Macroscopic analysis of the laser marks did not show any difference and further analysis has to be carried out to observe the print pattern. Further, the samples shown in the figure are only a part of the plaque, remaining parts used for microscopy and specialised wear testing respectively. SEM was carried out on all the samples to investigate the surface morphology of marking. Initial examination of the micrographs indicates that the laser marks result from localised foaming of the plastic material. Figure 4.15 shows the micrograph sheet of titanium dioxide additive at different compositions (T1-T5) marked at different power (A1-A5) and frequency settings (B1-B5). Similar micrograph sheets of the remaining additives are included in the Appendix for reference (Section 8.1, page no. 106-113).

The effect of percentage of additive, power and frequency on the laser mark can be clearly seen from the micrograph sheets and it can be confirmed that additives showing better contrast (i.e., T, A, SG and F) exhibit a decrease in the porosity up to 0.6 - 0.8% and then an increase in size of holes at 1.0%, indicating the optimum weight percentage for blending is 0.6-0.8%. Increase in the composition of the additive, up to 0.8%, might have improved the heat absorption and distribution ability of the compound, dissipated from the laser, which assisted in generating a surface mark with less porosity. Further increase in additive composition to 1.0% might have saturated the heat absorption capability, the extra heat over reacted with the material and resulted in a surface mark with higher porosity. The heat absorption of a material which depends on the specific heat capacity of the various additives is an important factor which effects the laser-material interaction, is discussed later in this section and also in section 4.4.3.



Laser Marking Parameters (A) - Pulse Rate 18MHz; Power 30-50%



Laser Marking Parameters (B) - Pulse Rate 15-35MHz; Power 35%

Figure 4-14 Digital photograph showing the Iriodin blended laser marked samples.

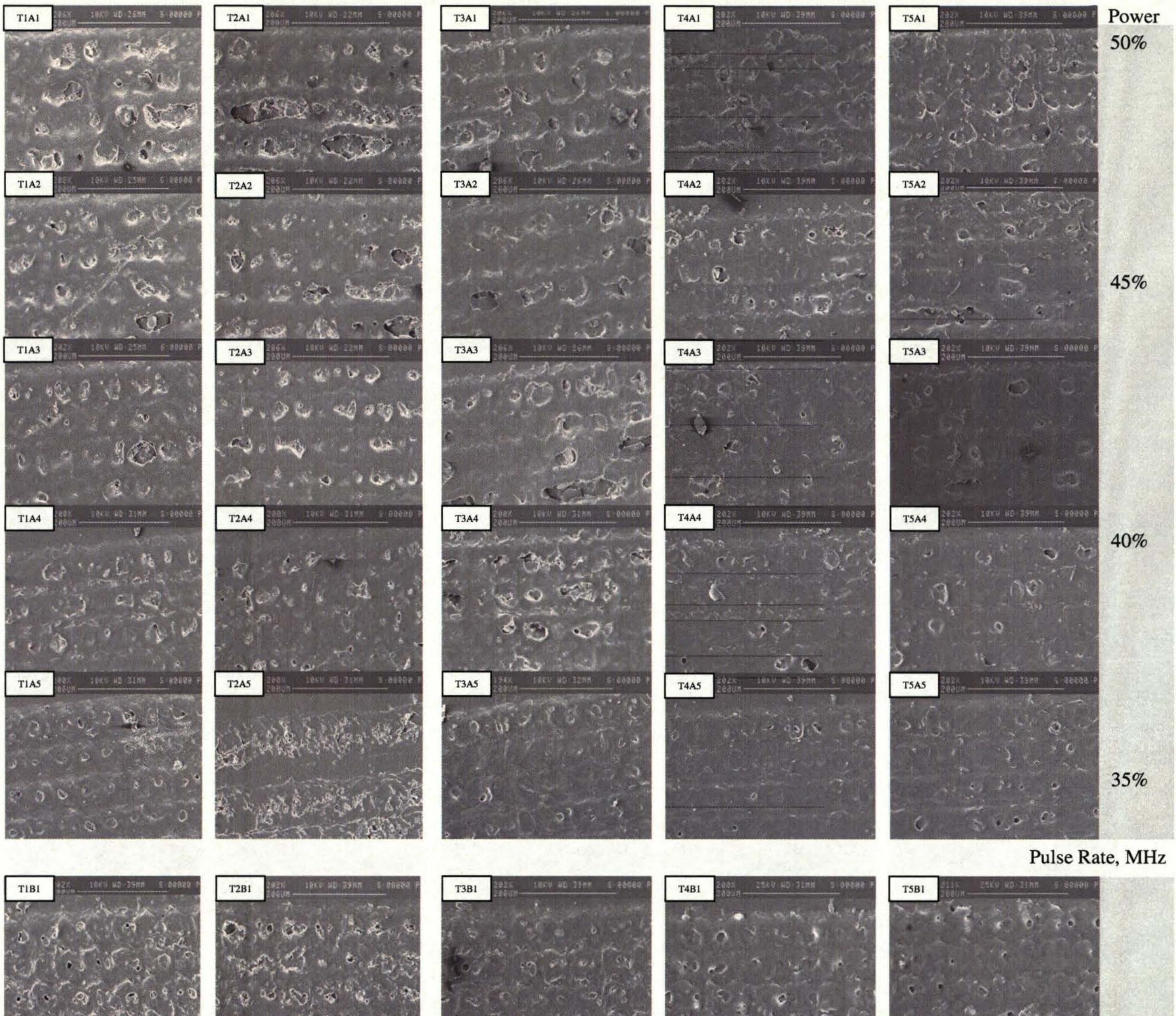


Figure 4-15 Micrograph sheet of Titanium dioxide, 200X.

Samples marked with high frequency or pulse rate and high power settings on laser show a uniform laser mark with little to no porosity due to melting and re-solidification of the surface. Further, interpreting the data of 600 samples from batch I is a demanding task, so to simplify the task all the micrographs are closely examined and ranked according to the following characteristics:

- Level of Marking &
- Percentage Porosity

Factors such as foam formation with a raised or shallow appearance and proximity of the laser spots are taken into account to decide the level of marking on the surface of the compound marked by a laser. Therefore, laser spots coinciding at their circumference which appear to be raised and marked by foaming mechanism would be considered as good level of marking. Further, partial to complete melting and re-solidification of the surface due to the overlap of laser spots appear to be raised but it is regarded as low level of marking because of its poor strength levels. Finally, if good level of marking is ranked 1 and low level of marking is ranked 5 the intermediate surface marks which are in the transition zone are rated accordingly on a scale of 1 to 5.

Percentage porosity as the name indicates would consider the number of pores, the size of the pores and their density to decide the rank. Micrographs were closely examined and the pore sizes measured in a few cases varied between 2-25mm, evenly distributed or segregated in one place in certain cases. Consequently, surface marks with less number of evenly distributed pores and small pore sizes are considered less porous which are ranked 1 and the marks with high porosity segregated at one place are ranked 5. So, size of the pores and their distribution are the key factors considered to rank the micrographs under the percentage of porosity category. Further, on a scale of 1 to 5, marks in the transition zone are ranked accordingly. Ranking is given for both the characteristics individually on a scale of 1 to 5, where 1 is given to good marks or low porosity and 5 for low marking levels and high porosity. Further, the overall rank of a sample is the sum of the two numbers given accordingly. Therefore, lower numbers or better ranks indicate that the samples possess good level of marking with low porosity and vice versa.

T: Titanium dioxide; A: Alumina trihydroxide; SG: Silver Coated Glass; F: Iron Oxide; IR: Iriodin; NMB: NMB Material;

Table 4.3 shows the ranks of additives such as T, A, SG and F with different compositions marked at different laser parameters which are compared with IR and NMB. The remaining additives including AZ, MV, MP and MM are listed later in table 4.4. Finally, samples with better ranks or smaller numbers which signify good marking and less porosity are identified and recommended for future formulations.

Samples	**Laser Marking Parameters / Rank**									
	A1	**A2**	**A3**	**A4**	**A5**	**B1**	**B2**	**B3**	**B4**	**B5**
T1	5	5	5	**3**	**3**	**3**	4	7	6	6
T2	6	6	5	4	6	5	6	6	6	4
T3	4	6	6	6	**3**	4	6	6	5	4
T4	4	5	5	5	4	4	6	6	5	4
T5	4	5	4	4	4	5	5	6	5	6
A1	5	5	5	4	**3**	**3**	6	7	6	6
A2	5	5	5	5	4	4	6	6	6	5
A3	4	5	5	5	**3**	**3**	6	5	5	5
A4	**3**	5	6	5	**3**	**3**	6	6	6	6
A5	6	6	6	5	**3**	**3**	5	6	6	5
F1	5	4	4	4	4	**3**	5	6	6	5
F2	5	4	**3**	4	4	4	4	4	5	5
F3	5	4	4	**3**	4	**3**	4	5	6	5
F4	4	4	**3**	4	4	**3**	5	6	5	5
F5	4	5	4	4	4	**3**	5	5	4	5
SG1	6	6	6	4	5	**3**	6	6	5	4
SG2	5	4	5	4	**3**	4	4	5	6	5
SG3	6	6	5	4	**3**	4	4	6	5	6
SG4	5	4	4	**3**	**3**	**3**	5	6	4	6
SG5	6	6	5	4	**3**	**3**	4	6	6	4
IR1	4	5	5	5	5	**3**	5	5	5	4
IR2	**3**	4	4	4	**3**	4	5	5	4	4
IR3	4	4	4	4	4	**3**	5	6	5	5
IR4	5	4	4	4	4	**3**	4	4	5	5
IR5	5	4	5	4	4	**3**	5	5	5	6
NMB	**3**	5	5	-	-	-	-	-	-	-

Table 4.3 Batch I formulation ranking for T, A, SG, F compared with IR and NMB.

T1-T5: 0.2-1.0% Titanium dioxide; A1-A5: 0.2-1.0% Alumina trihydroxide; SG1-SG5: 0.2-1.0% Silver Coated Glass
F1-F5: 0.2-1.0% Iron Oxide; IR1-IR5: 0.2-1.0% Iriodin; NMB- NMB Keyboard Material
A1-A5: 30-50% Power and 18MHz Frequency; B1-B5: 15-35MHz Frequency and 35% Power

Figure 4.16 shows the micrographs of 0.2% titanium dioxide, 0.2% silver coated glass, 0.6% iron oxide and 0.6% aluminium trihydroxide respectively, laser marked at 35MHz and 35% power setting, which secured rank 3. Each of these micrographs exhibits similar type of surface marking which is rugged and slightly porous, could be considered as good level of marking.

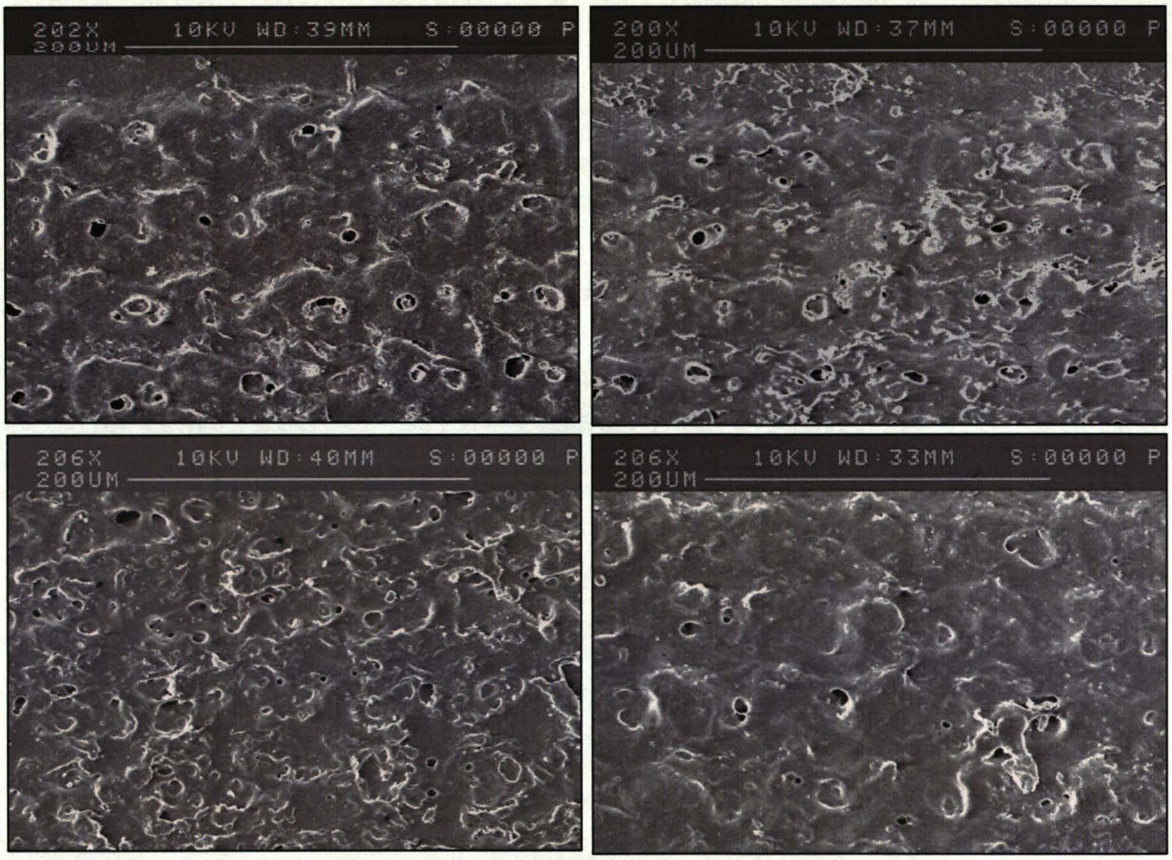


Figure 4-16 Micrographs showing the laser-material interaction (a) T1B1 (b) SG1B1 (c) F3B1 (d) A3B1

Ranks for samples AZ, MM, MP and MV are shown in table 4.4 and all the samples with a rank more than 3 indicate that they are potentially unsuitable for laser marking. Additives such as AZD and Mica showed poor contrast. AZD which is a popular blowing agent [7] is expected to promote foaming but the resulting compound is brittle and the anticipated foam texture is not observed under the SEM. Three different grades of mica are used for compounding. One grade,

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[7] Laser Marking on Plastics Materials, www.rofin-basel.com visited in January 2004, Rofin-Basel, USA.

T1B1: 0.2% TiO_2; 35% Power; 35MHz Frequency; SG1B1: 0.2% SCG; 35% Power; 35MHz Frequency

F3B1: 0.6% Fe_2O_3; 35% Power; 35MHz Frequency; A3B1: 0.6% Al_2O_3; 35% Power; 35MHz Frequency

AZ: Azodicarbonamide; MV: Micafil; MP: Phlogopite Mica; MM: Muscovite Mica; IR: Iriodin; NMB: NMB Keyboard Material

Mica-Vermiculite is expected to produce foam with 30% increase in volume [8], compared to parent material, on application of heat. Nonetheless, no such foaming is observed. This might be due to the low specific heat of AZD, 84 J/kg.K[17], and the Mica related additives, ranging between 21-84 J/kg.K[17]. The very high heat input on the low specific heat compounds caused the material to overheat which caused melting and re-solidification of the surface and finally generated brittle and porous laser marks.

Sample Name	Laser Marking Parameters (A or B) / Rank									
	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5
AZ1	6	6	5	4	4	6	5	5	5	6
AZ2	5	6	6	4	5	4	6	5	5	5
AZ3	5	5	5	5	4	4	5	5	5	5
AZ4	6	7	6	6	4	5	6	6	6	5
AZ5	5	6	6	5	4	6	5	5	4	4
MV2	6	6	5	4	4	4	4	7	5	5
MV5	6	6	5	5	4	4	6	6	6	5
MP1	4	6	5	5	4	4	5	7	7	6
MP2	5	6	5	5	4	4	7	6	6	5
MP3	6	6	5	6	4	4	6	6	6	6
MP4	5	5	5	5	5	5	6	6	6	6
MP5	6	5	5	4	4	5	5	5	5	5
MM1	5	5	5	5	4	5	5	6	7	5
MM2	5	5	5	4	4	4	6	7	6	5
MM3	5	5	5	4	4	4	6	5	5	5
MM4	5	5	5	5	4	4	5	6	6	4
MM5	5	5	5	4	5	4	5	5	6	5
IR1	4	5	5	5	5	**3**	5	5	5	4
IR2	**3**	4	4	4	**3**	4	5	5	4	4
IR3	4	4	4	4	4	**3**	5	6	5	5
IR4	5	4	4	4	4	**3**	4	4	5	5
IR5	5	4	5	4	4	**3**	5	5	5	6
NMB	**3**	5	5	-	-	-	-	-	-	-

Table 4.4 Batch I formulation ranking for AZ, MV, MP, MM compared with IR and NMB.

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[8] Sabreen, S.R., New Technologies of High Speed Colour Laser Marking of Plastics, in Plastics Decorating Mag. 2005, Peterson Publications.

[17] Brydson, J.A., Plastic Materials. 4th ed. 1999: Butterworth Scientific publication, page no.119-150.

AZ1-AZ5: 0.2-1.0% Azodicarbonamide; MV1-MV5: 0.2-1.0% Micafil; MP1-MP5: 0.2-1.0% Phlogopite Mica

MM1-MM5: 0.2-1.0% Muscovite Mica; IR1-IR5: 0.2-1.0% Iriodin; NMB- NMB Keyboard Material

A1-A5: 30-50% Power and 18MHz Frequency; B1-B5: 15-35MHz Frequency and 35% Power

The compounds incorporated with Merck's laser sensitive additive show little improvement in contrast and only the NMB keyboard material shows a clear white high contrast mark, figure 4.17. The micrograph of 0.6% Merck Compound (figure 4.17a) laser marked at 35MHz, 35% power shows a good level of marking with moderate porosity. Further, the micrograph of NMB compound (figure 4.17b) laser marked at 18MHz, 50% power settings show a good and uniform mark. Even though the laser mark shows a foamed plain surface rather than a cellular structure with no porosity, contrast of the mark is good indicating that the laser material interaction is a combination of colour change and foaming mechanism.

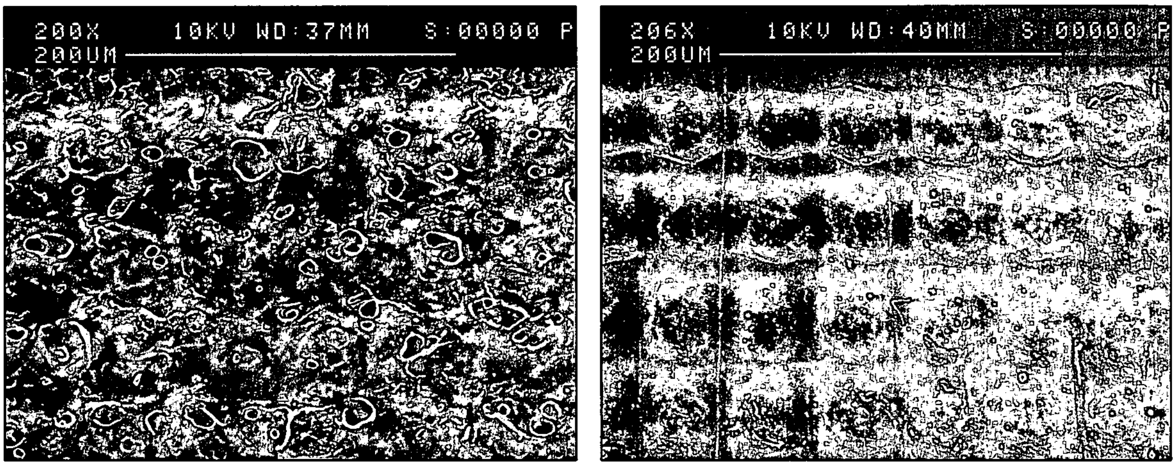

Figure 4-17 Micrographs showing the laser-material interaction in (a) IR3B1 (b) NMB1A1.

All the samples described above are tested for durability using the specialised wear tester. The results show that all the specimens have more than 30-40% loss in the printed character and consequently failed the test. Digital photography was carried out and figure 4.18 shows the iron oxide (F) samples which are laser marked and wear tested. These results relate to the first stage of investigation with the objective of developing an increased understanding of the laser-material interaction and the effect of a range of different additives. It is hoped that this knowledge will enable recommendations for further successful laser markable formulations.

IR3B1: 0.6% Iriodin, 35% Power, 35MHz Frequency; NMB1B1: 0.6% NMB, 35% Power, 35MHz Frequency
F1-F5: 0.2-1.0% Iron Oxide; A1-A5: 30-50% Power and 18MHz Frequency; B1-B5: 15-35MHz Frequency and 35% Power

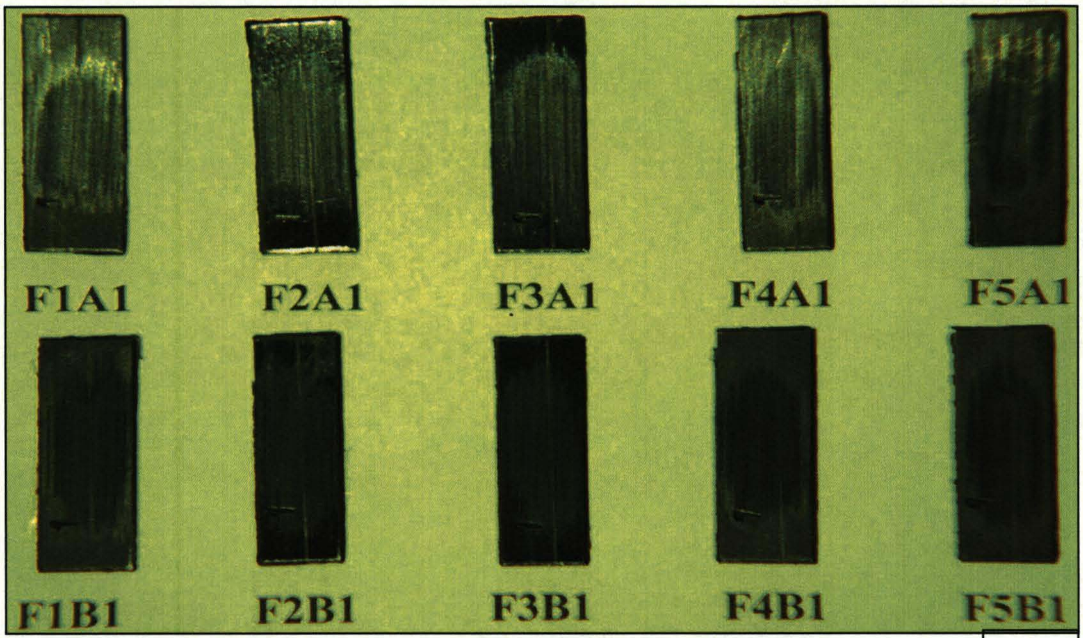

Figure 4-18 Samples showing more than 30-40% wear after the specialised wear test.

4.2.5 Recommendations from Batch I Formulations

Formulations with T, A, F and SG have generated surface marks which are less porous and good level of marking when compared with the other additives such as AZ, MV, MP and MM. Further, it can also be observed that the additives T, A, F and SG with absorption wavelengths in the range of 300-600nm (refer table 2.5) are the better performers among the batch I formulations in terms of porosity and markability. From table 4.3, it can be observed that with the maximum number of rank 3's aluminium trihydroxide has performed better than all the other additives and would be recommended as a main constituent for future compounding with additive combinations. Further, all the samples failed the specialised wear test but markability of the formulation could be improved by varying the composition, blending more than one additive to combine the best of both worlds and finally by optimising the laser marking parameters.

Identifying samples with good markability is a complicated task which is simplified by ranking them. Examining the micrograph sheets and the rank table indicate that the optimum level of mixing additives is 0.6-0.8% after which the pore size increased and reduced the quality of marking. Laser marking parameters such as power and frequency also play a major role in

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T: Titanium dioxide; A: Alumina trihydroxide; SG: Silver Coated Glass; F: Iron Oxide; S: Silicon; B: Bone char determining the interaction characteristics. Yet again, close examination of the micrographs indicate that marking is good at higher power and frequency settings. Therefore, marking at higher power settings of up to 80% and maintaining the frequency at 25-35MHz would give an increased understanding of the laser markable characteristics.

4.3 Formulation: Batch II

Compounding of new laser markable samples is carried out with a combination of additives recommended from the previous batch. Aluminium trihydroxide (A) was blended with titanium dioxide (T), iron oxide (F) and silver coated glass (SG) at different compositions with base material ABS. Silicon (S) with a band gap of 1.1eV and absorption wavelength of 1100nm, Bone char (B) which basically consists of calcium carbonate should give off carbon dioxide due to decomposition at higher temperatures, produced by the laser energy, leaving white coloured calcium oxide as the residue, were also mixed with ABS. Table 4.5 shows the compositions of different additives and the sample names.

Sl. No.	Additive	% Additive / Sample Name			
		0.3	0.6	1.0	1.5
1	Silicon dioxide (S)	S1	S2	S3	S4
2	Bone char (B)	B1	B2	B3	B4
	Additive Combinations	**0.6**		**0.8**	
3	**0.6%** Aluminium trihydroxide (A) and Titanium dioxide (T)	AT1		AT2	
4	**0.6%** Aluminium trihydroxide (A) and Iron oxide (F)	AF1		AF2	
5	**0.6%** Aluminium trihydroxide (A) and Silver coated glass (SG)	AS1		AS2	

Table 4.5 Compositions of additives used for Batch II formulations.

4.3.1 Laser Marking of Batch II Formulations

Marking of the samples was carried out by Thinklaser Systems and Specialist Services at the settings shown in figure 4.19. Samples S1, S2, B1, B2, AT1, AF1 and AS1 are marked at

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S1-S4: 0.3-1.5% Si; B1-B4: 0.3-1.5% Bone Char; AT1-AT2: 0.6% Al_2O_3 + 0.6-0.8% TiO_2; AF1-AF2: 0.6% Al_2O_3 + 0.6-0.8% Fe_2O_3; AS1-AS2: 0.6% Al_2O_3 + 0.6-0.8% Silver Coated Glass; C1-C4: 25MHz, 50-80% Power; D1-D4: 35MHz, 50-80%

25MHz frequency setting (C) and at increments in the power by a factor of 10 between 50-80% (1-4). The remaining samples (S3, S4, B3, B4, AT2, AT3 and AT4) are marked at the same power settings but at 35MHz (D) frequency.

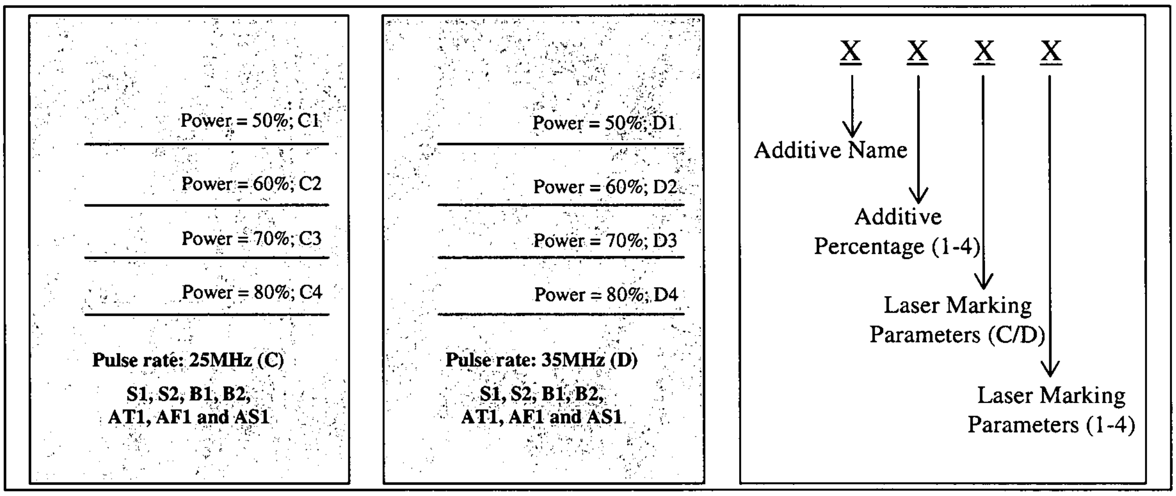


Figure 4-19 Plaques showing the outline of laser marks and sample naming procedure for batch II formulations.

4.3.2 Microscopic Analysis of Batch II Formulations

Laser marks generated on the samples have shown a good level of marking and less porosity. The micrographs are closely examined and ranked according to the guidelines given earlier in section 4.2.4. Table 4.6 shows the ranking of the different compounds in the batch II formulations. From the table it is evident that all the samples marked at 35MHz frequency setting have shown low level of marking, with ranks greater than 3, apart from the silicon power additive which attained the maximum number of rank 3. Low level of marking implies surface marks were larger in area with higher porosity, and this phenomenon has been explained clearly in section 4.2.4.

Samples marked at 25MHz showed a comparatively better mark at 50% and 60% power setting. Increase in power setting to 70% has increased the amount of porosity followed by melting and re-solidification of the surface at 80% with no porosity. This phenomenon can be clearly seen in micrographs of the AS1 samples shown in figure 4.20. An increase in the level of marking or the percentage of craters formed can be observed with the increase in power or frequency or even the percentage of additive to a certain level followed by partial to complete melting and reformation of the surface which makes it flat. This is observed even in the remaining samples and the micrograph sheets are included in the Appendix-II (Section 8.2, page no. 114-117).

Sample name	Laser Parameter (C) / Rank				Sample names	Laser Parameter (D) / Rank			
	C1	C2	C3	C4		D1	D2	D3	D4
S1	3	3	5	5	S3	3	5	6	5
S2	3	3	6	4	S4	3	3	4	5
B1	3	4	5	5	B3	4	4	6	5
B2	4	3	5	4	B4	4	5	6	4
AT1	3	3	6	5	AT2	4	4	6	5
AF1	3	5	6	5	AF2	3	4	6	6
AS1	3	3	6	5	AS2	4	4	6	5

Table 4.6 Ranking table for Batch II formulations.

Samples blended with Silicon (S) and Bone char (B) generated less porosity and show a good level of marking at 60% power and 25MHz frequency. Micrographs of the 0.6% silicon and 0.6% bone char marked at the settings given above are shown in figure 4.21, which depict a series of linear striations to form the mark which can be associated to the 6-ray laser head output.

Formulations with titanium dioxide, iron oxide and silver coated glass in combination with aluminium trihydroxide have shown improved markability and less porosity. Evidence for this can be seen in figure 4.22 which shows the micrographs of aluminium trihydroxide (A3) from batch I formulations and AT, a combination of A and T from batch II formulations. These materials have been marked at 25MHz with power levels set at 35% and 50% respectively.

S1-S4: 0.3-1.5% Si; B1-B4: 0.3-1.5% Bone Char; AT1-AT2: 0.6% Al_2O_3 + 0.6-0.8% TiO_2; AF1-AF2: 0.6% Al_2O_3 + 0.6-0.8% Fe_2O_3; AS1-AS2: 0.6% Al_2O_3 + 0.6-0.8% Silver Coated Glass; C1-C4: 25MHz, 50-80% Power; D1-D4: 35MHz, 50-80%

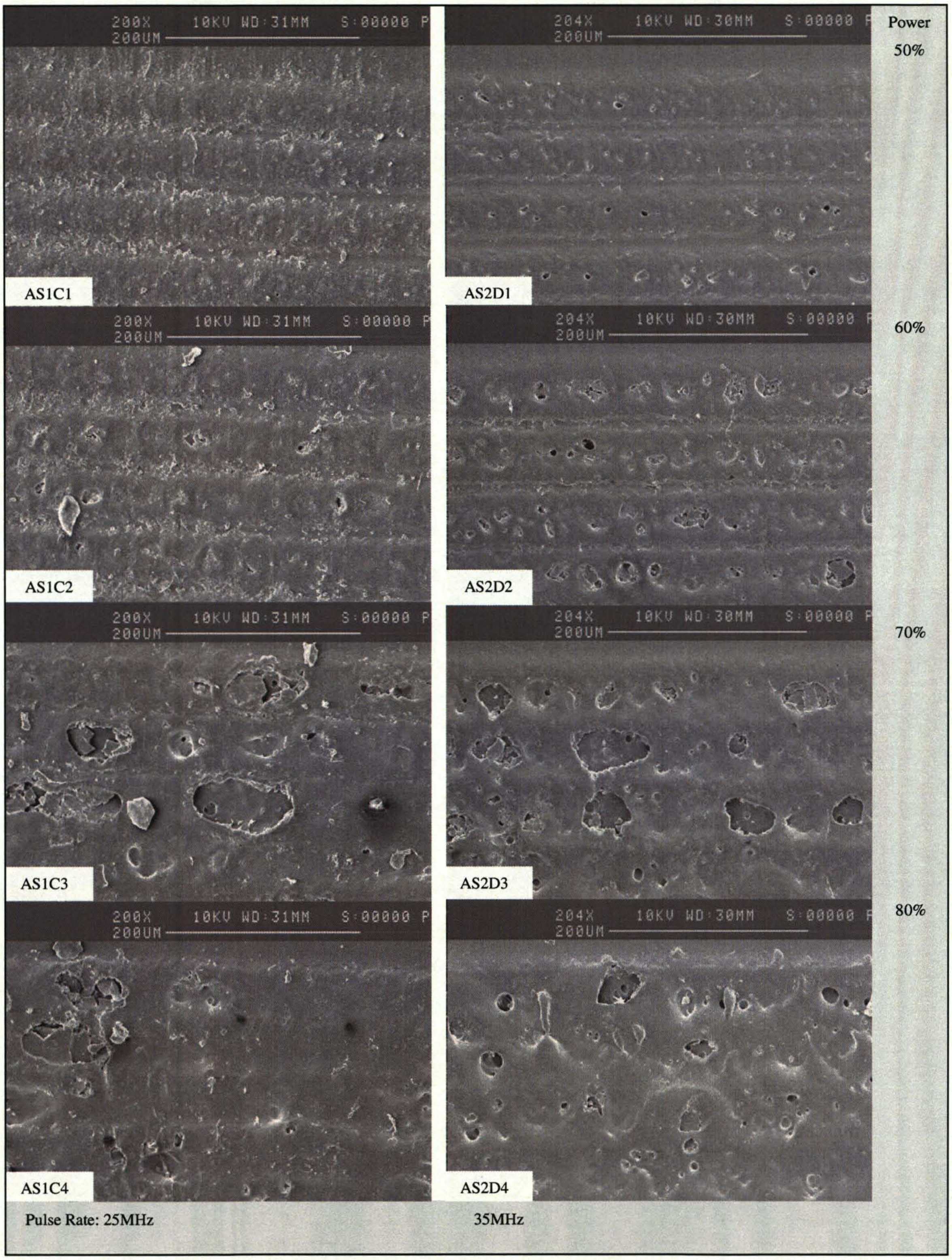


Figure 4-20 Micrograph sheet of 0.6% Alumina trihydroxide and 0.6% Silicon (AS1).

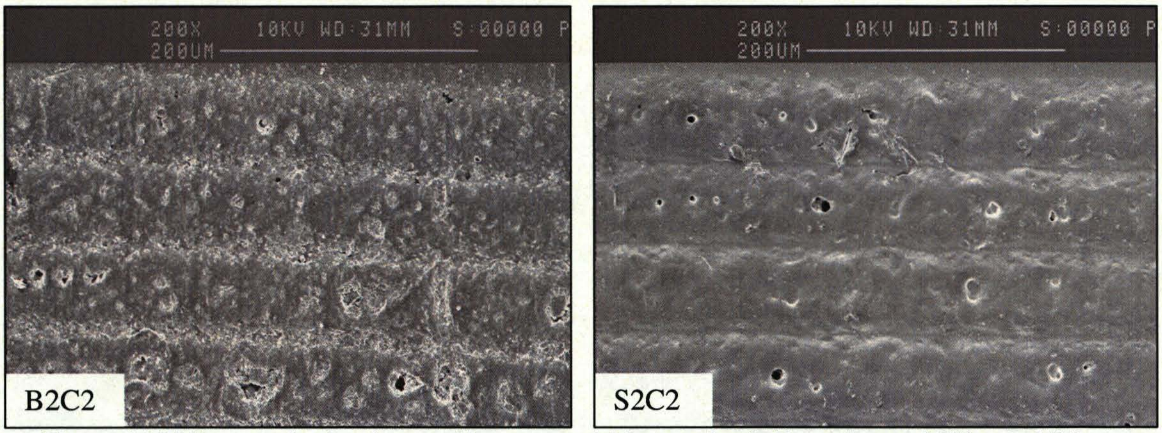


Figure 4-22 Micrographs showing good laser-material interaction in Bone char and Silicon additives.

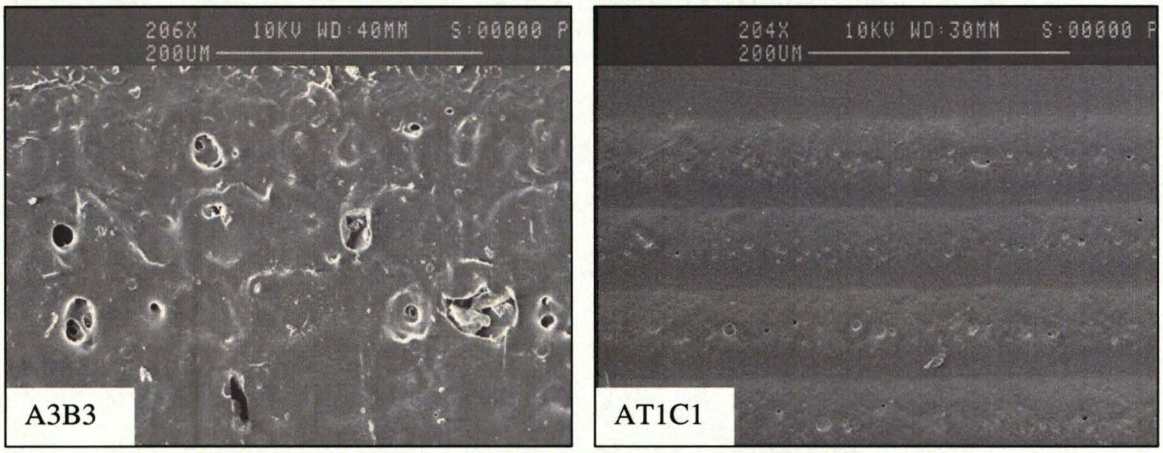


Figure 4-21 Micrographs showing the difference in marking between A3B3 and AT1C1.

4.3.3 Recommendations from Batch II Formulations

All the additives from batch II have shown laser-material interaction with improved markability and less porosity when compared to the batch I formulations but only when using particular laser marking settings. Therefore, optimisation of laser marking conditions is possible form the ranking table of batch II. 60% power and 25MHz frequency (P60F25) setting seem to be ideal for marking the samples. Further, additives including A, T and S with absorption wavelengths of 388nm, ≈400nm and 1100nm respectively have shown intense laser-material interaction and could be recommended for further studies.

B2C2: 0.6% Bone char; 25MHz Frequency; 50% Power; S2C2: 0.6% Silicon; 25MHz Frequency; 50% Power
A3B3: 0.6% Al_2O_3; 35% Power; 25MHz; AT1A1: 0.6% Al_2O_3 + 0.6% TiO_2; 50%Power; 25MHz Frequency

4.4 Formulations: Batch III

Previous formulations and analysis confirmed additives such as aluminium trihydroxide, titanium dioxide, silicon and bone char on their own, or in combination with other additives have shown intense laser-material interaction. The laser marks show good markability and less porosity when compared to the remaining additives from batch I and II. Therefore, in the third and final batch of micro-size additives, aluminium trihydroxide (A) and titanium dioxide (T) are formulated on their own and also in combination with silicon (S) and bone char (B) at different compositions as shown in table 4.7.

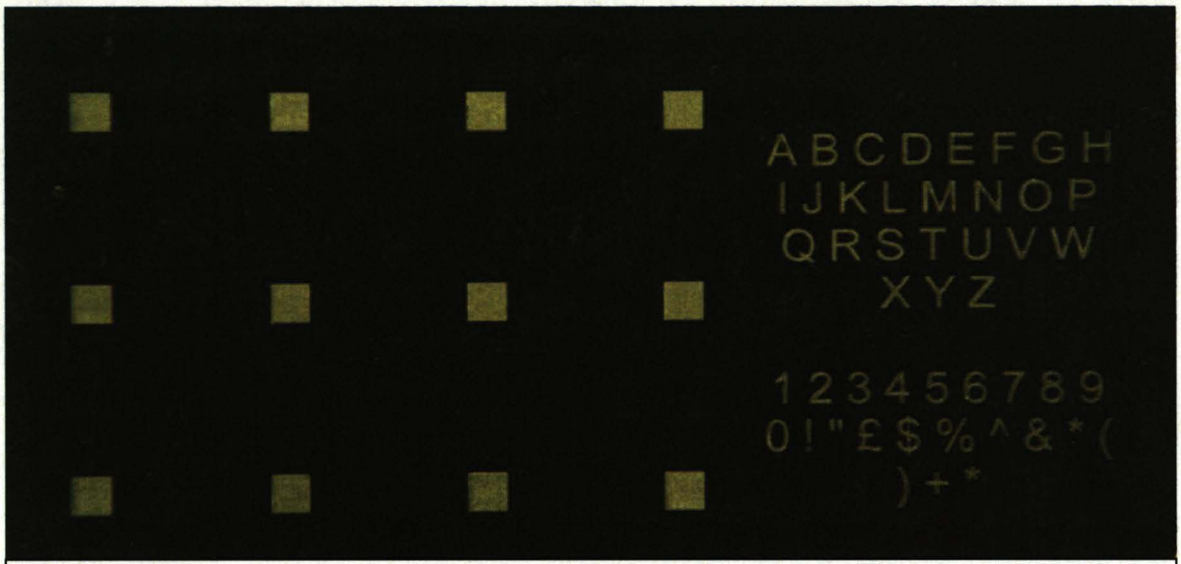
In recent times, there is a trend in driving the use of nano-materials[31] for improving mechanical properties of the compounds. Nano-additives such as Nano titanium dioxide (NT), Nano zinc oxide (NZ) and Nano copper oxide (NC) are used to produce nano-compounds. This will assist in understanding the affect of nano-additives in laser marking when compared with the normal micro-additives. Sample nomenclature for the nano compounds is also shown in table 4.7.

Sl. No.	Micro-additives	% Additive / Sample Name		
		0.6	1.0	
1	Aluminium trihydroxide (A)	A1	A2	
2	Titanium dioxide (T)	T1	T2	
Micro-additive combinations		**0.3**	**0.6**	
3	**0.6%** Aluminium trihydroxide (A) and Bone Char (B)	BA1	BA2	
4	**0.6%** Titanium dioxide (T) and Bone char (B)	BT1	BT2	
5	**0.6%** Aluminium trihydroxide (A) and Silicon (S)	SA1	SA2	
6	**0.6%** Titanium dioxide (T) and Silicon (S)	ST1	ST2	
Nano-additives		**0.05**	**0.1**	**0.2**
7	Nano Titanium dioxide (NT)	NT1	NT2	NT3
8	Nano Zinc oxide (NZ)	NZ1	NZ2	NZ3
9	Nano Copper oxide (NC)	NC1	NC2	NC3

Table 4.7 Nomenclature of Batch III formulations.

4.4.1 *Laser Marking of Batch III Formulations*

Samples were marked at the settings recommended from previous batch i.e. 60% power and 25MHz frequency (P60F25) settings. The design of marking is set up in accordance with the recommendations from section 4.1.4 (figure 4.9). A 1.0% aluminium trihydroxide (A2) laser marked plaque is shown in figure 4.23.



Laser Mark Setting (P60F25)
Power: 60%; Frequency: 25MHz; Speed of Marking: 1000mms^{-1}

Figure 4-23Aluminium trihydroxide (A2) plaque laser marked at P60F25 setting.

Further, the test plaques are also subjected to a different type of marking scheme in a grid-like pattern[32], as shown in figure 4.24. Specifically the 5x5mm squares are marked by varying the speed of marking on the y-axis followed by changing the frequency in increments of 4 between 4 and 24 (A-F) along the x-axis. Samples are laser marked at two different speeds 250 mms^{-1} (1) and 1000 mms^{-1} (2). This would enable the effect of speed of marking and laser light frequency to be investigated.

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[31] AS Edelstein, RC Cammarata and AE Edelstein, Nano-materials: Synthesis, Properties and Applications 1998, CRC Press and Publications, ISBN 07500739.

[32] Scott R Sabreen, Special focus on Decorating Plastics(Part 1-4) 2004, www.sabreen.com, The Sabreen Group, Inc., USA

The laser employed at Thinklaser Systems and Services is an Nd:YAG type. This is excited using a lamp pump which makes it difficult to change the power and frequency settings at the same time. Consequently power settings are fixed at 60%. Figure 4.24 shows the BT1 (0.3% bone char and 0.6% titanium dioxide) grid marked at the settings given above. Considering the entirety of the total number of samples naming them has been a complicated task and the nomenclature of grid-like pattern laser marked samples is shown in table 4.8.

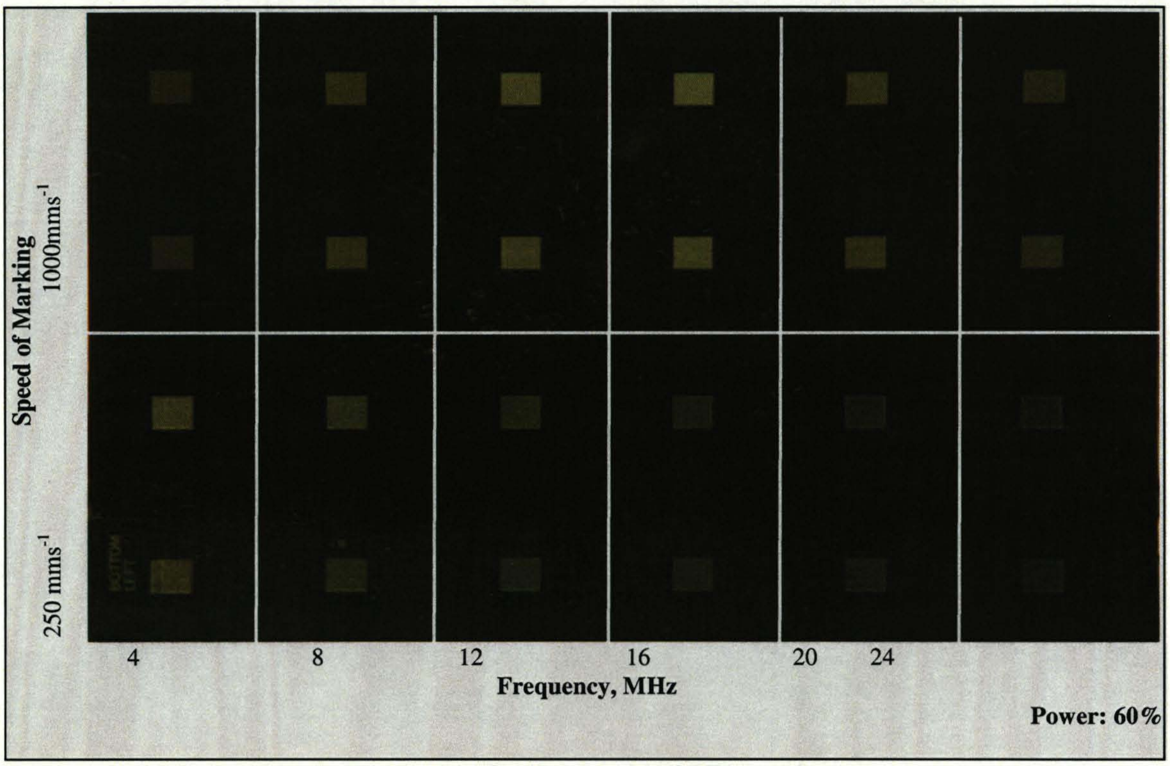
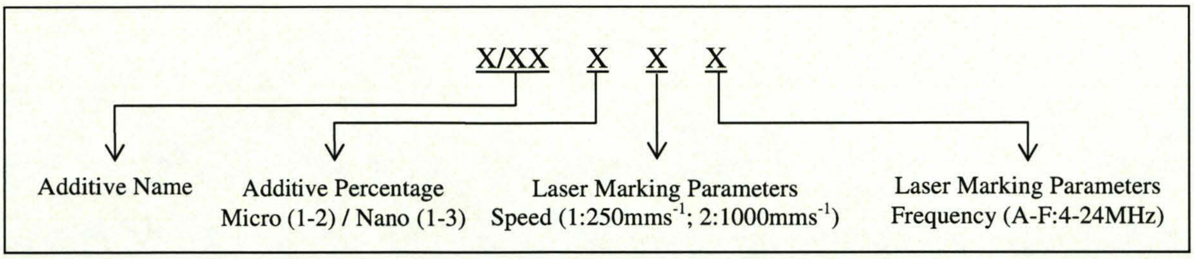


Figure 4-24 Grid laser marked BT1 sample.

4.4.2 *Testing of Laser Marked Samples*

A wide range of testing was carried out on the grid-like pattern and P60F25 laser marked samples which include the specialised wear test, chromometry, scanning electron microscopy and digital photography. Durability analysis which includes the unique test regime combining the affects of impact, sweat and light was carried out on the P60F25 laser marked samples. Analysis of the micro-additive and nano-additive compounds laser marked at two different settings, namely P60F25 and grid marking, is discussed under different sections for ease and clarity.



Freq.	**A (4MHz)**		**B (8MHz)**		**C (12MHz)**		**D (16MHz)**		**E (20MHz)**		**F (24MHz)**	
Speed	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**
NT1	NT11A	NT12A	NT11B	NT12B	NT11C	NT12C	NT11D	NT12D	NT11E	NT12E	NT11F	NT12F
NT2	NT21A	NT22A	NT21B	NT22B	NT21C	NT22C	NT21D	NT22D	NT21E	NT22E	NT21F	NT22F
NT3	NT31A	NT32A	NT31B	NT32B	NT31C	NT32C	NT31D	NT32D	NT31E	NT32E	NT31F	NT32F
NZ1	NZ11A	NZ12A	NZ11B	NZ12B	NZ11C	NZ12C	NZ11D	NZ12D	NZ11E	NZ12E	NZ11F	NZ12F
NZ2	NZ21A	NZ22A	NZ21B	NZ22B	NZ21C	NZ22C	NZ21D	NZ22D	NZ21E	NZ22E	NZ21F	NZ22F
NZ3	NZ31A	NZ32A	NZ31B	NZ32B	NZ31C	NZ32C	NZ31D	NZ32D	NZ31E	NZ32E	NZ31F	NZ32F
NC1	NC11A	NC12A	NC11B	NC12B	NC11C	NC12C	NC11D	NC12D	NC11E	NC12E	NC11F	NC12F
NC2	NC21A	NC22A	NC21B	NC22B	NC21C	NC22C	NC21D	NC22D	NC21E	NC22E	NC21F	NC22F
NC3	NC31A	NC32A	NC31B	NC32B	NC31C	NC32C	NC31D	NC32D	NC31E	NC32E	NC31F	NC32F
A1	A11A	A12A	A11B	A12B	A11C	A12C	A11D	A12D	A11E	A12E	A11F	A12F
A2	A21A	A22A	A21B	A22B	A21C	A22C	A21D	A22D	A21E	A22E	A21F	A22F
T1	T11A	T12A	T11B	T12B	T11C	T12C	T11D	T12D	T11E	T12E	T11F	T12F
T2	T21A	T22A	T21B	T22B	T21C	T22C	T21D	T22D	T21E	T22E	T21F	T22F
SA1	SA11A	SA12A	SA11B	SA12B	SA11C	SA12C	SA11D	SA12D	SA11E	SA12E	SA11F	SA12F
SA2	SA21A	SA22A	SA21B	SA22B	SA21C	SA22C	SA21D	SA22D	SA21E	SA22E	SA21F	SA22F
ST1	ST11A	ST12A	ST11B	ST12B	ST11C	ST12C	ST11D	ST12D	ST11E	ST12E	ST11F	ST12F
ST2	ST21A	ST22A	ST21B	ST22B	ST21C	ST22C	ST21D	ST22D	ST21E	ST22E	ST21F	ST22F
BA1	BA11A	BA12A	BA11B	BA12B	BA11C	BA12C	BA11D	BA12D	BA11E	BA12E	BA11F	BA12F
BA2	BA21A	BA22A	BA21B	BA22B	BA21C	BA22C	BA21D	BA22D	BA21E	BA22E	BA21F	BA22F
BT1	BT11A	BT12A	BT11B	BT12B	BT11C	BT12C	BT11D	BT12D	BT11E	BT12E	BT11F	BT12F
BT2	BT21A	BT22A	BT21B	BT22B	BT21C	BT22C	BT21D	BT22D	BT21E	BT22E	BT21F	BT22F
NMB	NM1A	NM2A	NM1B	NM2B	NM1C	NM2C	NM1D	NM2D	NM1E	NM2E	NM1F	NM2F
ABS	AB1A	AB1B	AB2A	AB2B	AB1C	AB2C	AB1D	AB2D	AB1E	AB2E	AB1F	AB2F
	Speed 1= 250mms^{-1}				**Speed 2= 1000mms^{-1}**				**Power = 60%**			

Table 4.8 Sample naming procedure and Nomenclature of grid laser marked samples of Batch III formulations.

4.4.3 Microscopic and Durability Analysis of Grid Marked Micro Compounds

Formulations with additives such as A, T, BA, BT, SA and ST recommended from the previous batches which were grid-like pattern laser marked samples are discussed in this section. Specialised wear testing and chromometry are carried out on these samples.

Effect of Laser Marking Parameters on A Compounds

Figure 4.25 shows the comparison of contrast values (E) for A, BA and SA grid laser marked at different frequencies and speeds. Laser marks at 4MHz frequency setting show the highest contrast value for 250mms^{-1} speed marking, followed by a sudden decrease in the contrast with an increase in the frequency. The 250 mms^{-1} speed allowed the laser to interact with the material more intensely and resulted in melting and re-solidification (reformation) of the surface. Increase in frequency increased the overlap of the individual laser spots which resulted in reformation of a plain flat surface. This has been shown to affect the initial contrast of the laser mark. Evidence for this is clearly shown in micrographs of the grid laser marked BA1 sample, shown in figure 4.26.

In this case the line of best fit is a curve, where the contrast values (ΔE) vary with frequency. This non-linearity between contrast and frequency indicate that there are more variables which play a role in deciding the relation. Hence, a best fit line or curve is a dependent on the data to determine the complex mathematical relationships between variables.

Laser marking at 1000mms^{-1} showed improved markability characteristics such as raised foam formation and generated high contrast marks when compared to the marks at 250mms^{-1}. Laser mark generated at 8MHz frequency setting shows the highest contrast, figure 4.25, followed by a slight decrease in the contrast measurements. For a laser marking speed of 1000mms^{-1}, the effects resulting from laser-material interaction at 4MHz is less obvious because the laser spots left large unmarked areas which resulted in a character with low contrast.

A1-A2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
T1-T2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

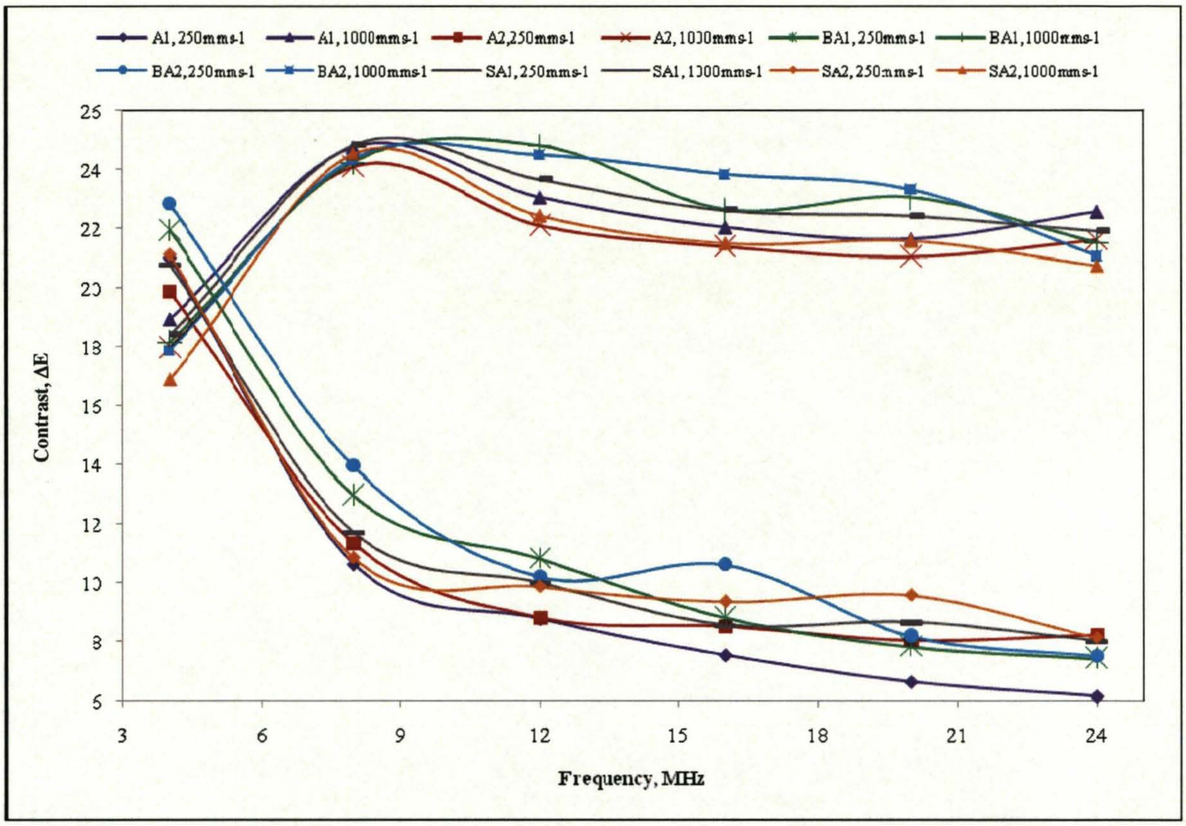


Figure 4-25 Graph showing the effect of frequency on contrast of grid marked A, BA and SA samples.

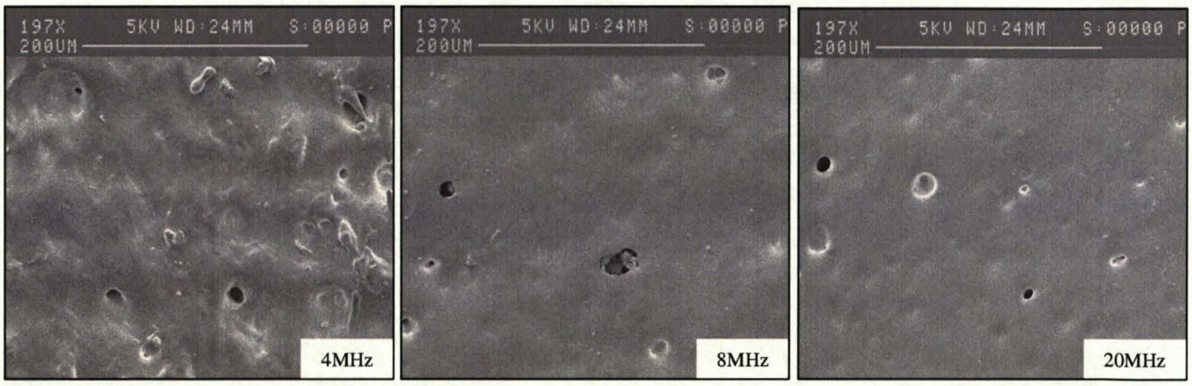


Figure 4-26 Micrographs showing the affect of frequency on contrast of BA1 grid marked samples at 250mms-1.

A1-A2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

Nevertheless at 8MHz, the laser-material interaction can be said to be optimised because the laser spots coincide precisely with each other at the circumference. This resulted in a laser mark with a higher degree of contrast when compared to the laser marks at higher frequency settings. Increase in the frequency led to an overlap of the laser spots and resulted in reformation of the surface and low contrast. Figure 4.27 shows the variation in surface morphology for different sets of laser marks and supports the explanation given above.

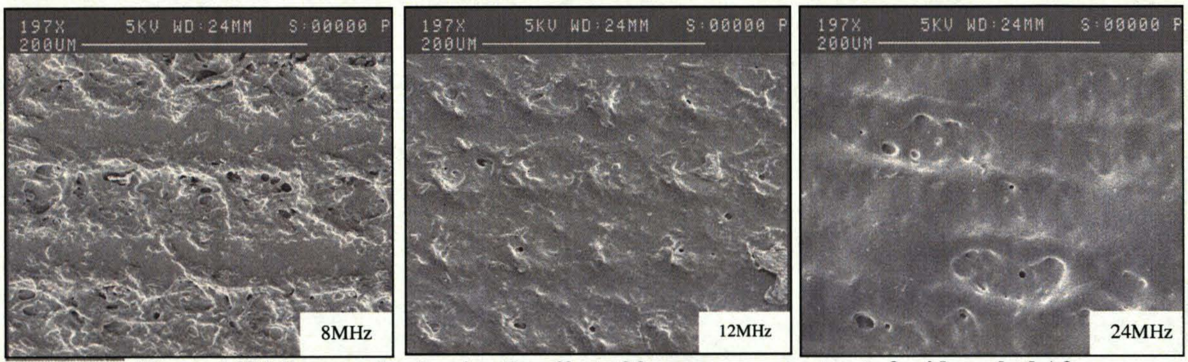


Figure 4-27 Micrographs showing the affect of frequency on contrast of grid marked A2 sample at 1000mms^{-1}.

Effect of Laser Marking Parameters on T Compounds

In the case of T, BT and ST grid marked samples, results obtained are of a similar nature to those described above. Figure 4.28 shows the variation in contrast with change in frequency at marking speeds of 250 and 1000mms^{-1} respectively. Figure 4.29 shows the micrographs of T1 samples grid laser marked at a speed of 1000mms^{-1} and at 4 different frequencies. This clearly demonstrates the changes in surface morphology of the laser marks. The separation of laser lines/spots on the 4MHz sample are far away with large areas left unmarked, which is the reason for low contrast. Increase in the frequency reduced the gap between the laser lines/spots which reflected the incident light diffusively and enhanced the contrast values.

However, with even higher values of frequency the laser lines/spots overlapped, leading to heavy interaction on the material and finally reformation of a plain surface which did not reflect the incident light diffusively and this resulted in lower contrast values.

A2: 1.0% Al_2O_3; T1-T2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

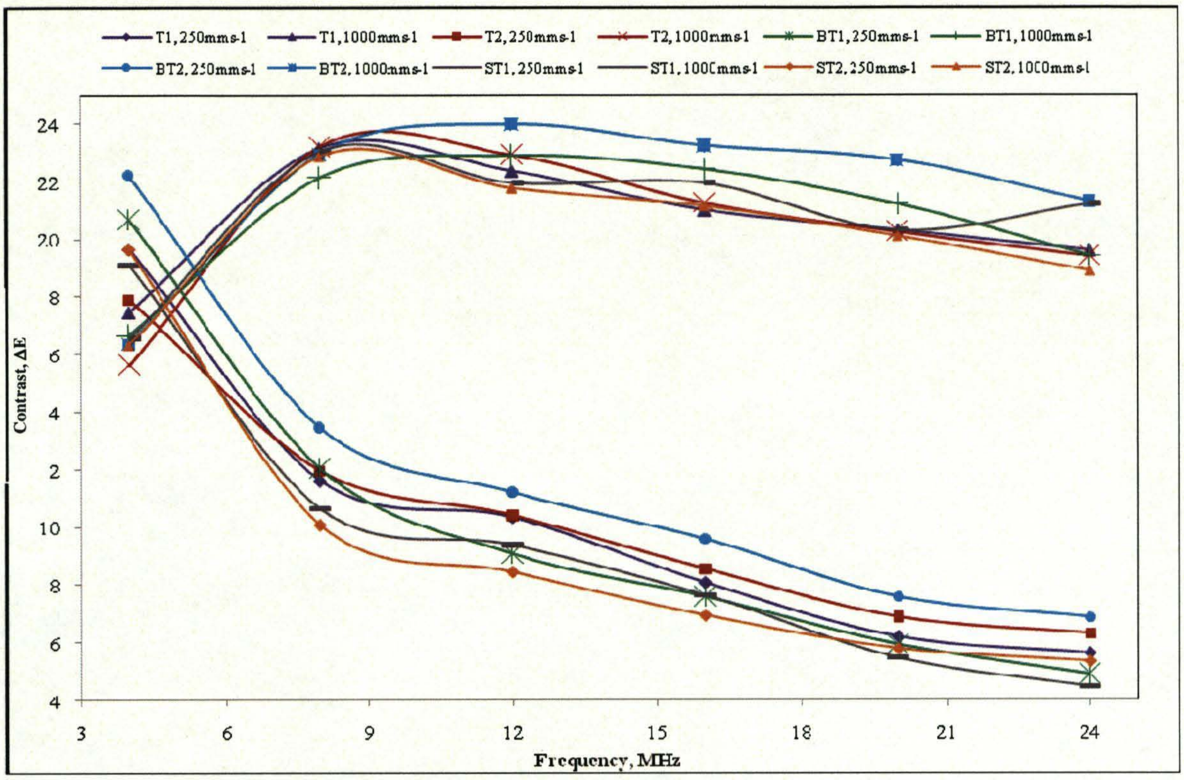


Figure 4-28 Graph showing the effect of frequency on contrast of grid marked TO, BT and ST samples.

Further, results from the specialised wear tests carried out on the A & T compounds are shown in table 4.9. Wear testing was carried out in stages of 500 cycles at a time, then the laser mark is examined. If the mark still remains another test cycle was carried out until the laser mark is completely removed. Therefore, cycle range indicates the laser mark is completely worn out without a trace during that test period. The results show that an increase in the frequency of the marking improved the life of the mark. This can be attributed to the discussion stated earlier; i.e., increase in frequency increased the level of laser-material interaction which might have also increased the depth of mark. Laser marks with increased depths would take more time to wear out and improve the life of the mark. Therefore, in order to improve the life of the laser mark higher frequency settings are preferred but, at the same time, contrast values are compromised.

A2: 1.0% Al_2O_3; T1-T2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

Finally, it can be recommended that an optimum frequency setting should be determined individually for each compound in order to generate good contrast and durability.

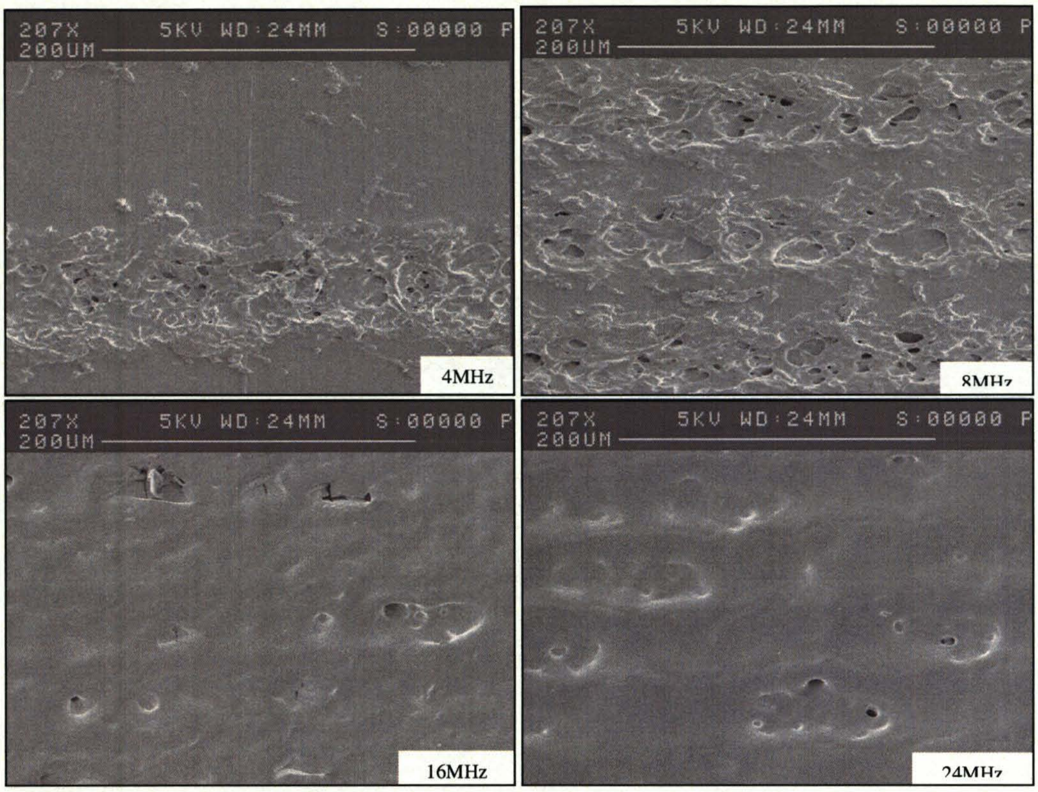


Figure 4-29 Micrographs showing the affect of frequency on contrast of grid marked T1 sample at 1000mms^{-1}.

Samples	Complete removal of laser mark, cycle range	Samples	Complete removal of laser mark, cycle range
SA12A	500-1000	**BT22A**	500-1000
SA12B	1500-2000	**BT22B**	1500-2000
SA12C	1500-2000	**BT22C**	1500-2000
SA12D	2500-3000	**BT22D**	1500-2000
SA12E	2500-3000	**BT22E**	1500-2000
SA12F	1500-2000	**BT22F**	1500-2000

Table 4.9 Results of Specialised wear test showing the effect of frequency.

A1-A2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
T1-T2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

Comparison of Micro Compounds with NMB and ABS

ABS and NMB plaques were also grid laser marked and serve as the boundaries of a scale for comparison with the other compounds. Figure 4.30 compares results for NMB and ABS, showing the effect of frequency on contrast of marks made on materials incorporating A, BA and SA additives. The plaques in this case were laser marked in a grid-like pattern at 1000mms^{-1}. From the figure 4.30 and table 4.10 it can be seen that there is a confirmed increase in the contrast values between ABS and its compounds. However, it proves to be a complicated task to study and understand the effect of increasing the concentration of the additive on the contrast of the laser marks. Compounds such as T, BT and ST also exhibit the same phenomenon, described above, when compared with NMB and ABS. Table 4.10 also shows the compounds with the highest contrast values, obtained when laser marked at 8Hz and 1000mms^{-1}.

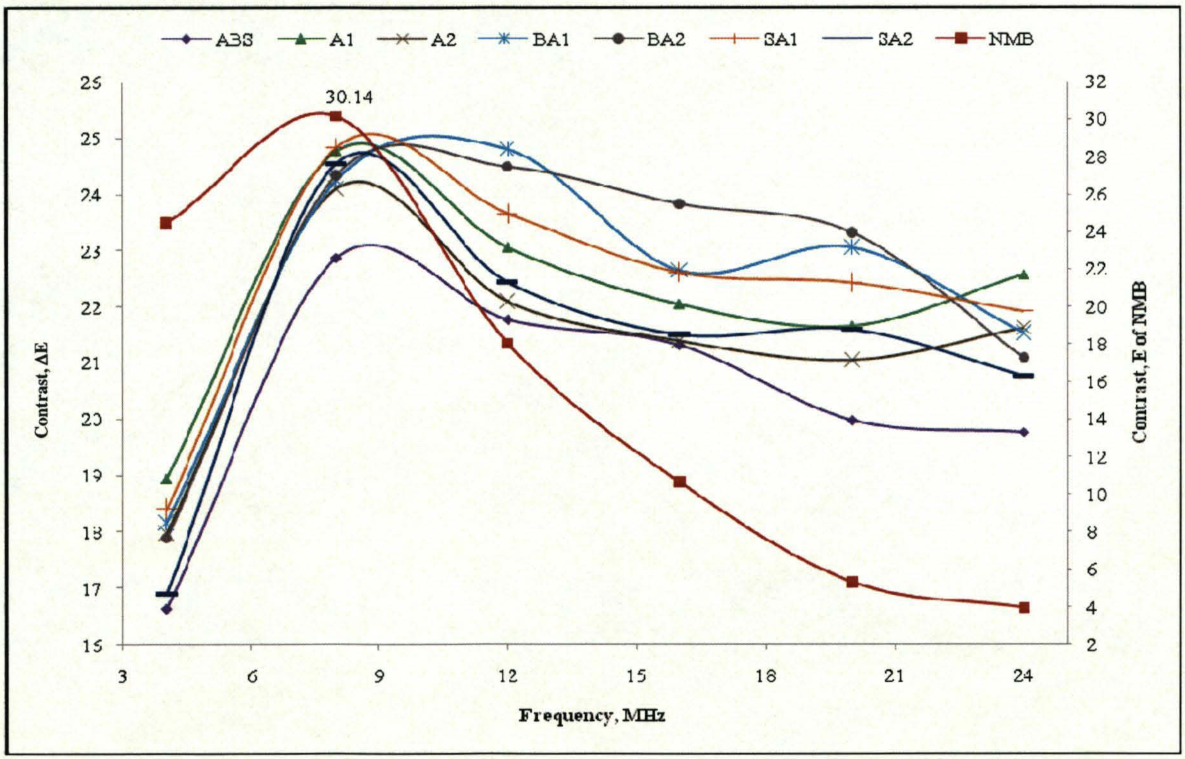


Figure 4-30 Graph showing the affect of frequency on contrast of NMB, ABS, A, BA and SA samples grid marked at 1000mms-1.

A1-A2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
T1-T2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

Sample	ABS	A1	A2	BA1	BA2	SA1	SA2	NMB
Contrast, E	22.87	24.76	24.1	24.24	24.34	24.3	24.54	30.14
Sample	**ABS**	**T1**	**T2**	**BT1**	**BT2**	**ST1**	**ST2**	**NMB**
Contrast, E	22.87	23.16	23.23	22.15	22.95	23.06	22.88	30.14

Table 4.10 Maximum contrast values of some samples grid marked at 8MHz and 1000mms^{-1}.

Results from the specialised wear test indicate that the average mark life of ABS and NMB is between 500-1000 and 4500-5000 cycles respectively. Even though most of the samples which possess high contrast failed the wear test, as shown in table 4.9, some samples marked at higher frequencies passed the test, indicating that an optimum frequency should be determined so that any laser marked character has the important attributes of high contrast and durability.

Effect of Micro additives Combinations on Markability

Compounds such as BA, BT, SA and ST produced by mixing bone char or silicon with A or T are discussed in this section. Figure 4.31 shows the contrast values of BA and BT compounds which indicate samples with aluminium trihydroxide (BA) possessed better contrast ($\Delta E \approx 24$, table 4.10) than BT ($\Delta E \approx 22$, table 4.10). Similarly, figure 4.32 shows that samples mixed with a combination of silicon and aluminium trihydroxide (SA, $\Delta E \approx 24$, table 4.10) possess better contrast than ST ($\Delta E \approx 23$, table 4.10). Specialised wear test results are shown in table 4.11. As mentioned previously, the cycle range to failure indicates that the laser mark is completely obliterated within that range. The results show that compounds with aluminium trihydroxide as an additive such as A, BA and SA materials possess longer mark lives with loss of laser mark in the 1500-2000 cycle range. In the case of samples with titanium dioxide as an additive such as T, BT and ST the mark life is less than 1000 cycles.

This might be due to the low specific heat of aluminium trihydroxide, 419 J/kg.K[17], which is much less than titanium dioxide, 711 J/kg.K[17]. The titanium based compounds with high specific heat require/absorb more energy to heat up, where less energy is required to heat the

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[17] Brydson, J.A., Plastic Materials. 4th ed. 1999: Butterworth Scientific publication, page no.119-150.

A1-A2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
T1-T2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1}Speed, 4-24MHz Frequency, 60% Power

aluminium trihydroxide based compounds. In the present case where the energy/heat input from the laser is constant, aluminium based compounds are heated up faster than the titanium based compounds and the remaining heat assists in producing a laser mark with extra depths, in the former. Finally deeper laser marks take more time to obliterate and hence the enhanced durability performance of aluminium based compounds.

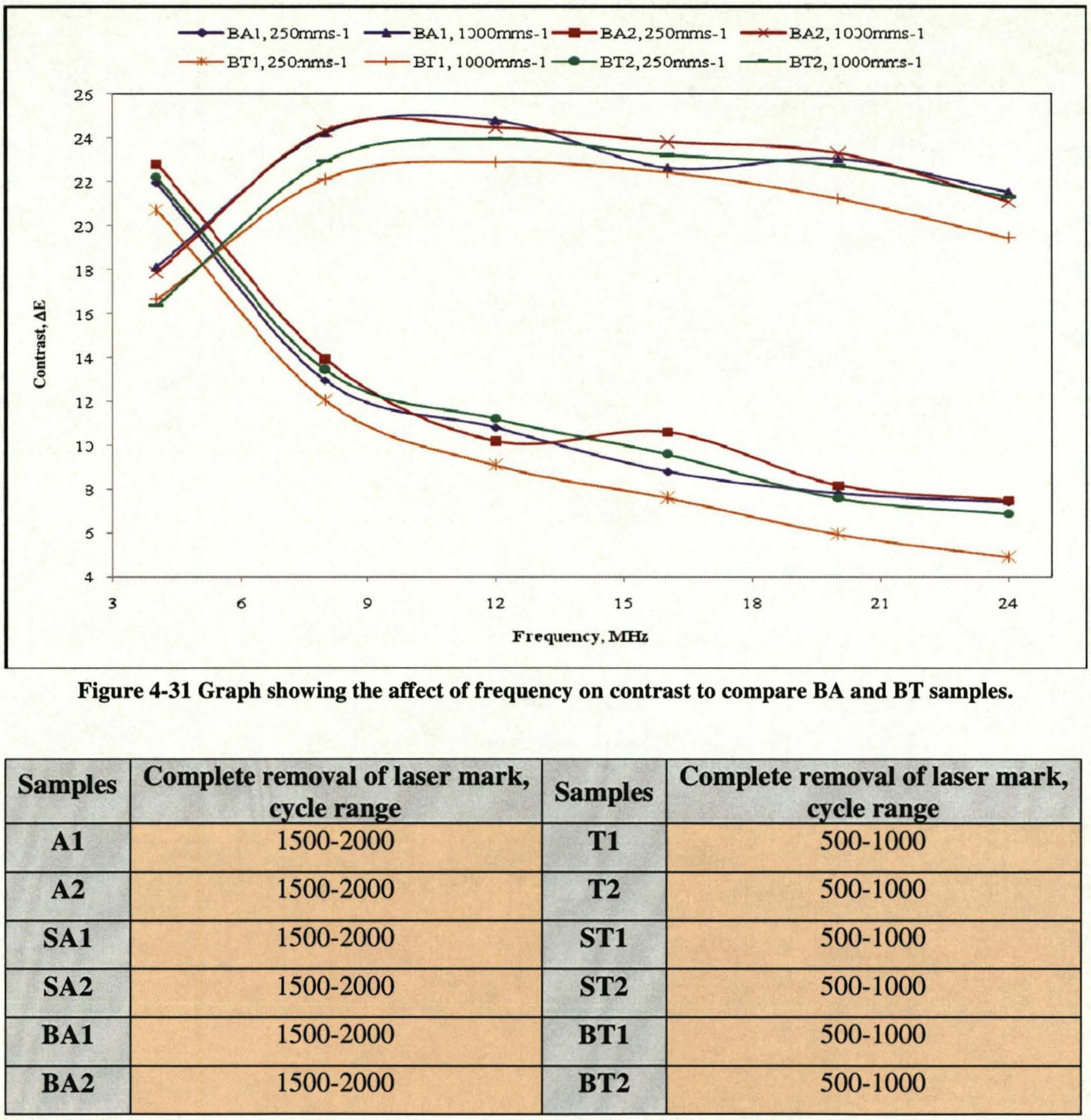

Figure 4-31 Graph showing the affect of frequency on contrast to compare BA and BT samples.

Samples	Complete removal of laser mark, cycle range	Samples	Complete removal of laser mark, cycle range
A1	1500-2000	**T1**	500-1000
A2	1500-2000	**T2**	500-1000
SA1	1500-2000	**ST1**	500-1000
SA2	1500-2000	**ST2**	500-1000
BA1	1500-2000	**BT1**	500-1000
BA2	1500-2000	**BT2**	500-1000

Table 4.11 Specialised wear test results of micro compounds.

A1-A2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
T1-T2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

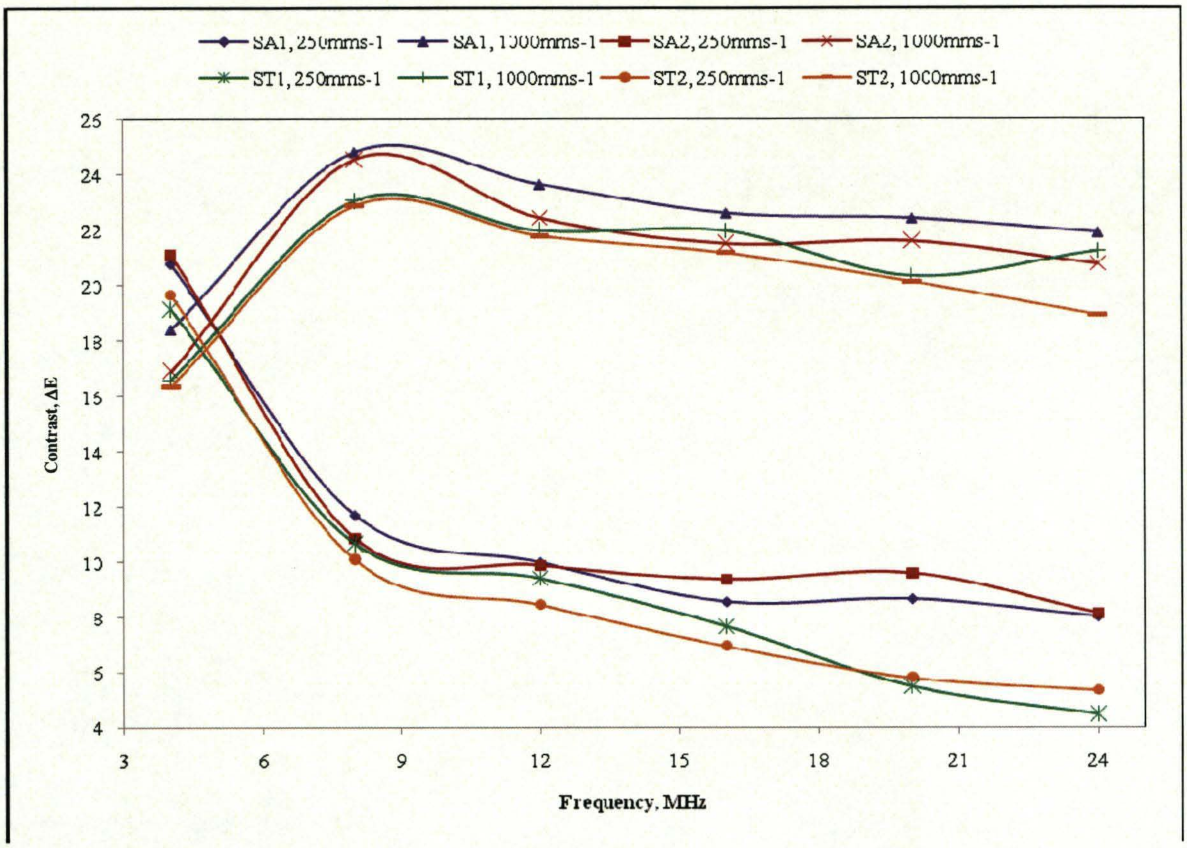

Figure 4-32 Graph showing the affect of frequency on contrast to compare SA and ST samples.

Figure 4.33 shows the micrographs of SA1 and ST1 compounds grid laser marked at a speed of 1000mms^{-1} and 8MHz frequency setting. The micrographs show that amount of unmarked area in ST12B sample is greater when compared to the SA12B, indicating that the markability at this given setting is better for the latter. Further, intense laser material interaction of the A group of compounds, compared to the T formulations, might be the reason for its better performance in terms of contrast values and wear tests. This suggests that aluminium trihydroxide might be one of the important additives which could be recommended for future compounding of laser sensitive materials.

A1-A2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
T1-T2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

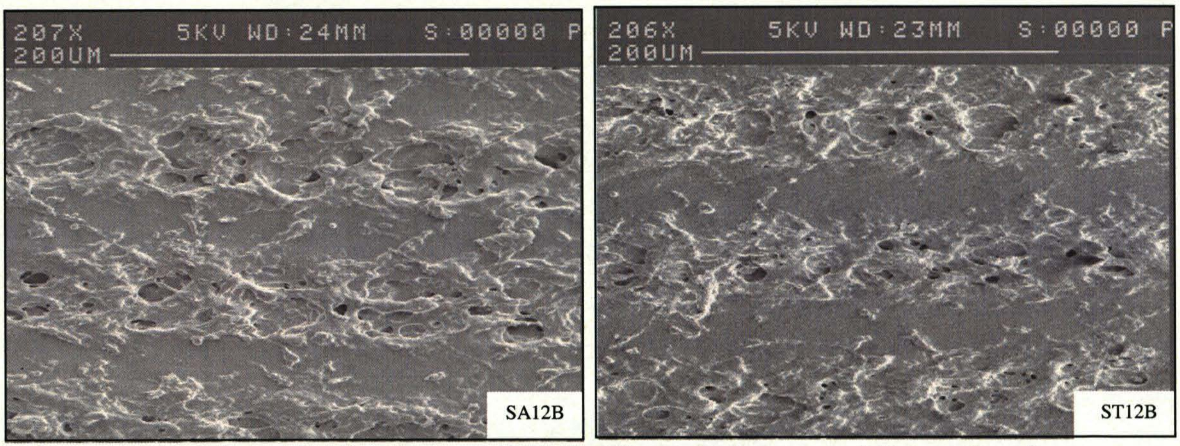

Figure 4-33 Micrograph showing the difference in laser material interaction of SA12B and ST12B samples.

4.4.4 *Microscopic and Durability Analysis of Grid Marked Nano Compounds*

Nano-materials have been influencing the material properties with its large surface area and small particle size[31]. Work has been undertaken to investigate the effect of the nano-additive surface area on laser marks of plastic materials. Nano compounds are laser marked at different settings, as stated earlier and this section considers grid laser marked samples. Specialised wear testing and chromometry were also carried out on these novel materials.

Effect of Laser Marking Parameters on Nano Compounds

Figure 4.34 illustrates the effect of frequency and laser speed on the contrast values of grid laser marked NT, NZ and NC at different compositions. All the samples produced improved contrast values when marked at a speed of 1000mms^{-1} and a frequency of 8MHz. Subsequent tests showed a gradual reduction in the contrast measurement with increasing frequency.

Marking at a speed of 250mms^{-1} the contrast is improved at 4MHz but it is followed closely by a sharp decrease as the frequency increases. These effects are similar to those seen with the micro-additive materials. This is further evidence confirming that the explanation given above, with regards to the decrease in contrast with the increase in frequency, holds true even in this case.

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[31] AS Edelstein, RC Cammarata and AE Edelstein, Nano-materials: Synthesis, Properties and Applications 1998, CRC Press and Publications, ISBN 07500739.

SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2

1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

The variation in surface morphology resulting from laser marking in nano zinc oxide (NZ) compounds, grid laser marked at 250mms^{-1} and different frequencies, can be seen in the micrographs shown in figure 4.35. The NZ21A sample, marked at 4MHz, exhibits improved contrast compared with the laser marks at higher frequencies in the series of 250mms^{-1}. This is indicative of intensified laser-material interaction. Increase in frequency to 8MHz reduced the distance between the laser spots and an even more intense level of interaction with the material resulted in a plane surface, as shown in sample NZ21B and this might be the reason for reduced contrast values.

Figure 4.36 shows similar variation in the laser mark of nano copper oxide compounds, grid laser marked at different frequencies and 1000mms^{-1} speed. The NC32B sample, marked at 8MHz, exhibited higher contrast measurements among all the NC3 samples marked at 1000mms^{-1}. The micrograph of NC32B shows a cellular structure which reflects incoming light effectively. This could explain the higher contrast values. Increase in frequency permitted melting and re-solidification of the material giving rise to a plain surface, as discussed in section 4.4.3, is a likely reason for low contrast in NC32E.

Specialised wear tests of NT1 nano compound are shown in table 4.12 which indicate that the durability of the mark increased initially and later decreased with an increase in frequency. The increase in the life of the mark might be due to more intense laser-material interaction which also influenced the depth of the mark. Further increase in the frequency is believed to have melted and re-solidified the surface which is brittle and lead to the earlier loss of the laser mark. Similar trends are seen in the other nano compounds, so optimising the frequency for laser marking each compound to generate characters with good contrast and durability is essential

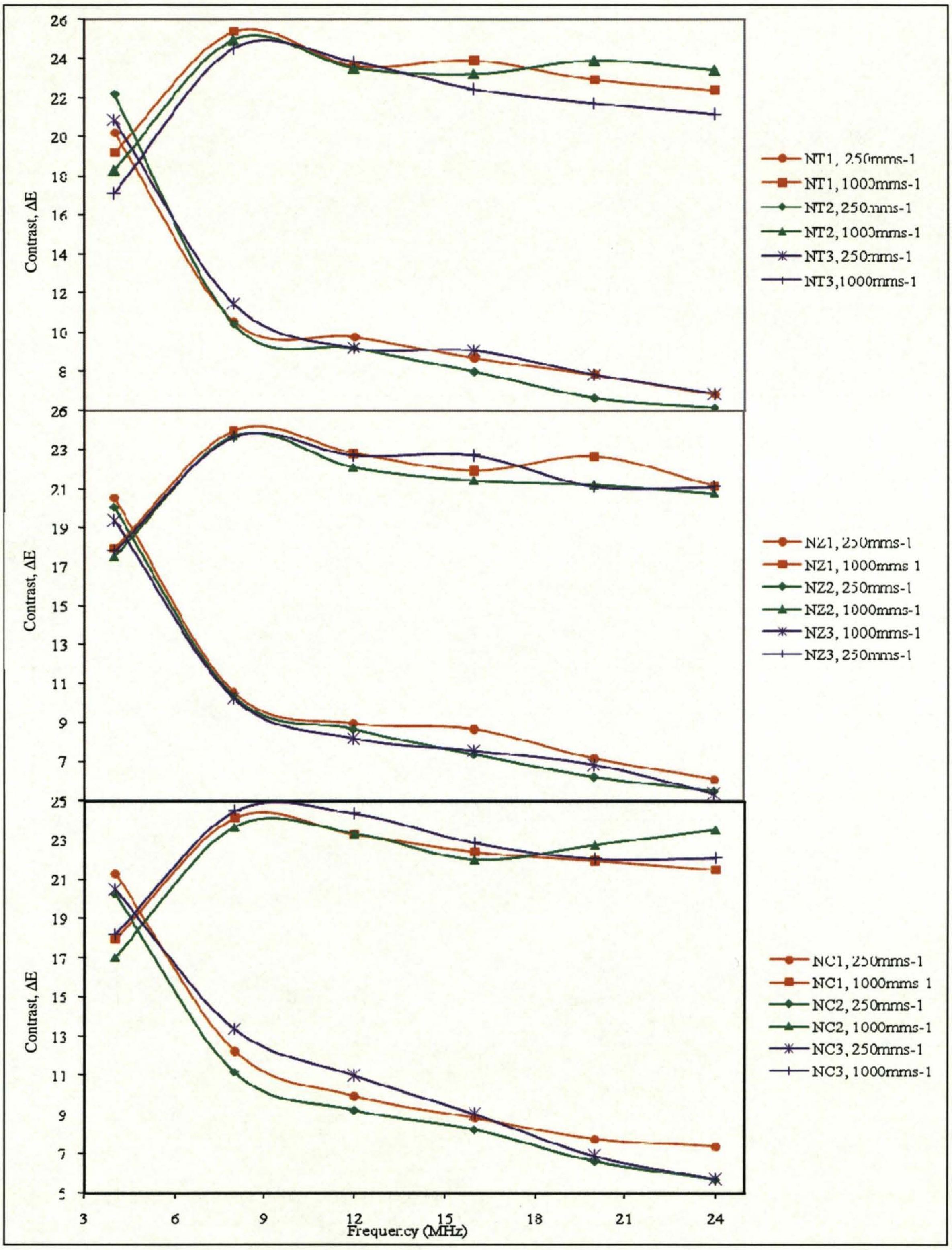
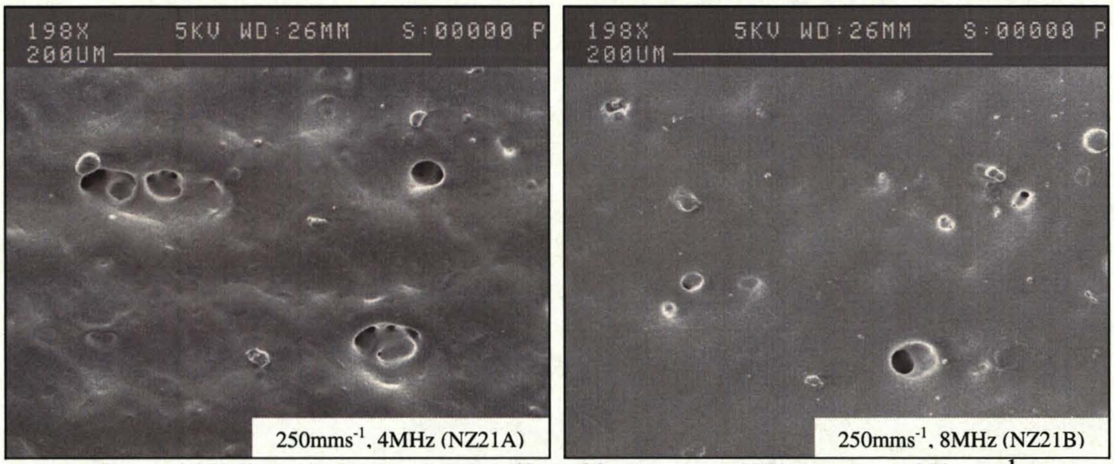


Figure 4-34 Graphs illustrating the effect of frequency and speed on contrast of different NT, NZ and NC samples.



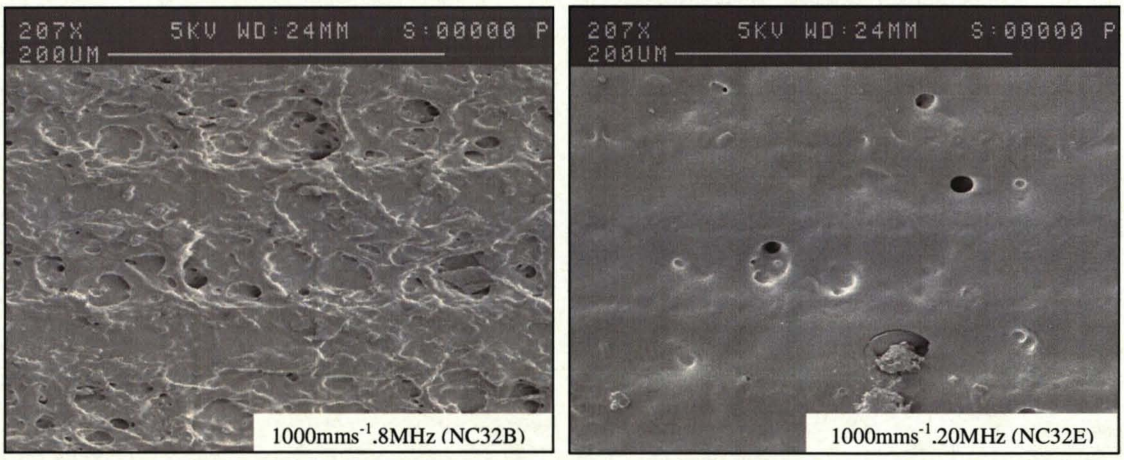
250mms^{-1}, 4MHz (NZ21A)

250mms^{-1}, 8MHz (NZ21B)

Figure 4-35 Micrographs showing the affect of frequency on NZ2 samples at 250mms^{-1}.

Sample	Complete removal of laser mark, cycle range
NT12A	500-1000
NT12B	500-1000
NT12C	1500-2000
NT12D	1500-2000
NT12E	500-1000
NT12F	500-1000

Table 4.12 Specialised wear test results of NT1 nano compound.



1000mms^{-1}.8MHz (NC32B)

1000mms^{-1}.20MHz (NC32E)

Figure 4-36 Micrographs showing the effect of frequency on NC3 samples marked at 1000mms^{-1}.

NT1-NT3: 0.05-0.2% Nano TiO_2; NZ1-NZ3: 0.05-0.2% Nano ZnO; NC1-NC3: 0.05-0.2% Nano CuO
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

Effect of Nano Additives on Markability

The effect of weight percentage of the additive in the compound on laser markability is shown in figure 4.37. Contrast values of NT and NZ decreased with an increase in additive concentration but surprisingly NC did not show a suitable relation. X-ray mapping was also carried out on the samples to confirm levels of additive dispersion and distribution throughout the bulk material. However, results from x-ray mapping (section no. 4.2.3, page no.50) show that the additive particles to be appropriately separated (i.e., no clusters or agglomeration) and distributed evenly throughout the surface. NT, NZ and NC grid laser marked at 8MHz and 1000mms^{-1}, which exhibited better contrast values, are shown in table 4.13 for reference, and compared with ABS and NMB.

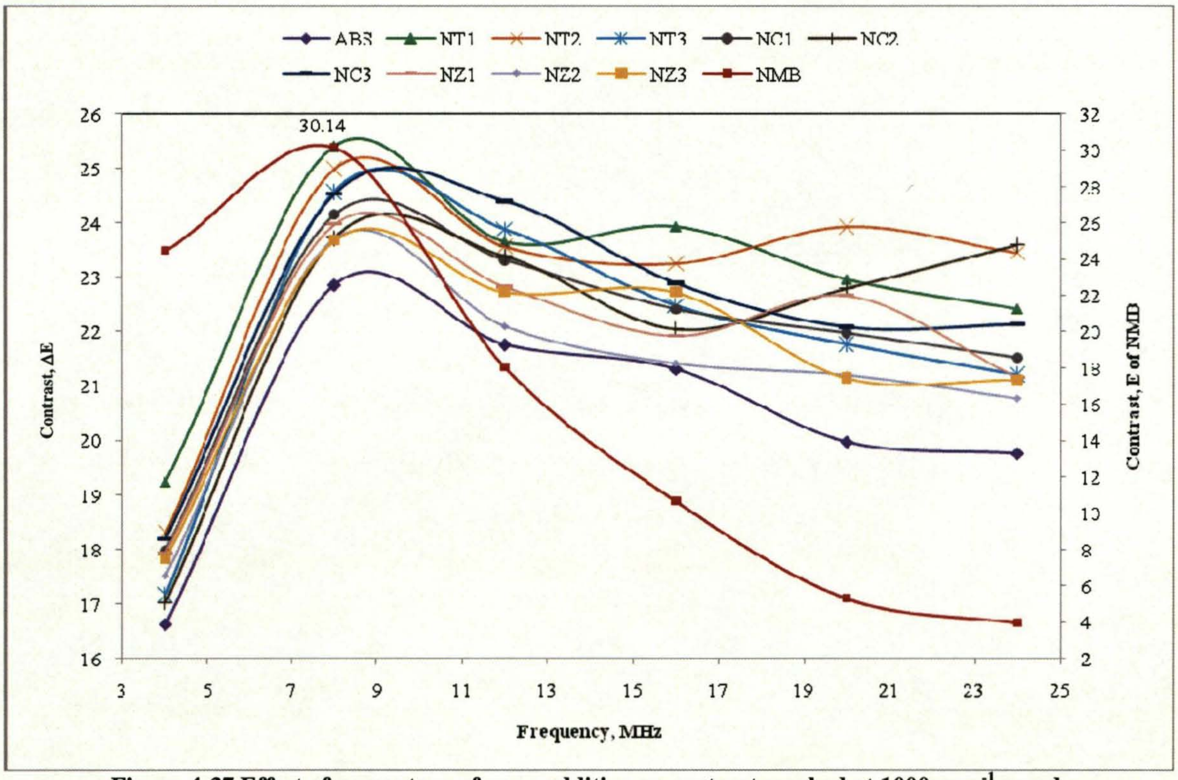


Figure 4-37 Effect of percentage of nano additive on contrast marked at 1000mms^{-1} speed.

NT1-NT3: 0.05-0.2% Nano TiO_2; NZ1-NZ3: 0.05-0.2% Nano ZnO; NC1-NC3: 0.05-0.2% Nano CuO
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

Additive	1	2	3
NT	25.40	25.00	24.57
NZ	23.98	23.71	23.68
NC	24.15	23.72	24.54
ABS	22.87	NMB	30.14

Table 4.13 Contrast of nano compounds compared to ABS and NMB marked at 1000mms^{-1} and 8MHz.

Examining the micrographs of NT1, NT2 and NT3 samples marked at 1000mms^{-1} and 8MHz frequency, figure 4.38, it can be confirmed that less intense interaction between the laser and base material has gradually increased the distance between the laser spot lines. This in turn has been shown, in the present work, to reduce the contrast values. Increase in additive percentages might have affected the light reflectance levels of the compound and hence resulted in reduction in level of marking which directly affects the contrast values.

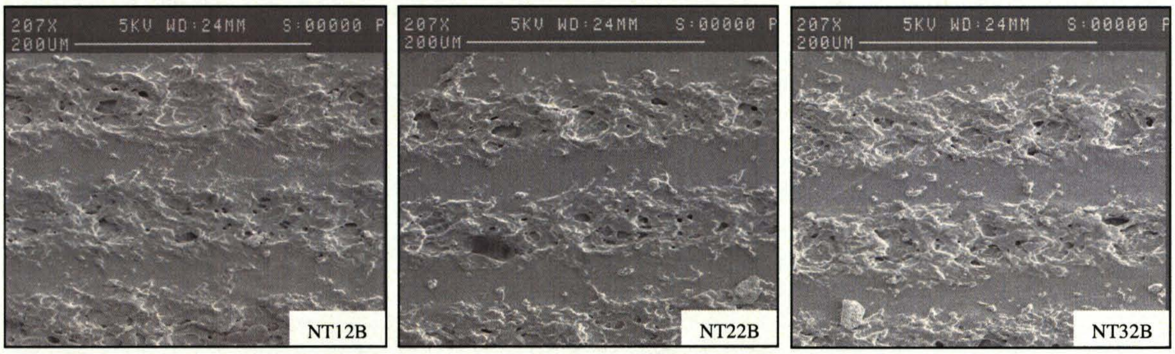


Figure 4-38 Micrographs of NT1, NT2, and NT3 compounds marked at 1000mms^{-1}, 8MHz.

From figure 4.37 and table 4.13, it can also be seen that NT12B, NZ12B and NC32B exhibit higher contrast values among the nano compounds in their respective groups. Micrographs of these samples are shown in figure 4.39. Even though NT12B has performed well with the highest contrast measurement of them all, micrographs show a uniform level of marking with no distinctive characteristic to explain its enhanced performance. However, factors such as percentage of porosity, spot size in the foam pattern and the ability to absorb light play a combined role and might have a direct effect on the markability and contrast of the laser mark.

NT1-NT3: 0.05-0.2% Nano TiO_2; NZ1-NZ3: 0.05-0.2% Nano ZnO; NC1-NC3: 0.05-0.2% Nano CuO
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

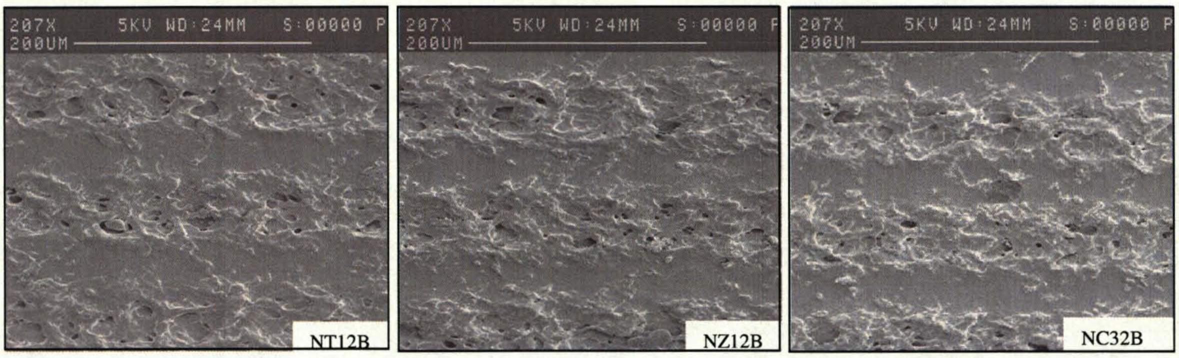


Figure 4-39 Micrographs of nano compounds marked at 1000mms^{-1}, 8MHz to show the affect additives.

Results from the wear testing of the nano compounds shown in table 4.14, indicate that increase in the percentage of the nano additive improved the life expectancy of the laser mark. However, from figure 4.37 it can be seen that contrast values decreased with an increase in percentage weight of the additive. This increase in the durability of the mark might be due to the increase in the depth of the mark. Therefore, optimising the frequency of the laser should be carried out to obtain a balance of contrast and durability.

Sample	Complete removal of laser mark, cycle range	Sample	Complete removal of laser mark, cycle range	Sample	Complete removal of laser mark, cycle range
NT12B	500-1000	**NZ12B**	500-1000	**NC12B**	500-1000
NT22B	500-1000	**NZ22B**	500-1000	**NC22B**	500-1000
NT32B	1500-2000	**NZ32B**	1500-2000	**NC32B**	1500-2000

Table 4.14 Results of the Specialised wear test of the nano compounds.

Comparison of Nano and Micro Additives

Finally, the performance of micro and nano compounds is compared in figure 4.40 which depicts the contrast values of titanium dioxide (T) and nano titanium dioxide (NT). The graph shows that contrast values of NT ($\Delta E \approx 25$, table 4.13) are higher than the T values ($\Delta E \approx 22$, table 4.10) which would appear to confirm that the high surface area of nano additives, compared to the micro-additives, is a factor and if an appropriate additive is optimised with different laser settings the compound could show high potential in terms of improved contrast for laser marked characters in dark materials.

NT1-NT3: 0.05-0.2% Nano TiO_2; NZ1-NZ3: 0.05-0.2% Nano ZnO; NC1-NC3: 0.05-0.2% Nano CuO
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1}Speed, 4-24MHz Frequency, 60% Power

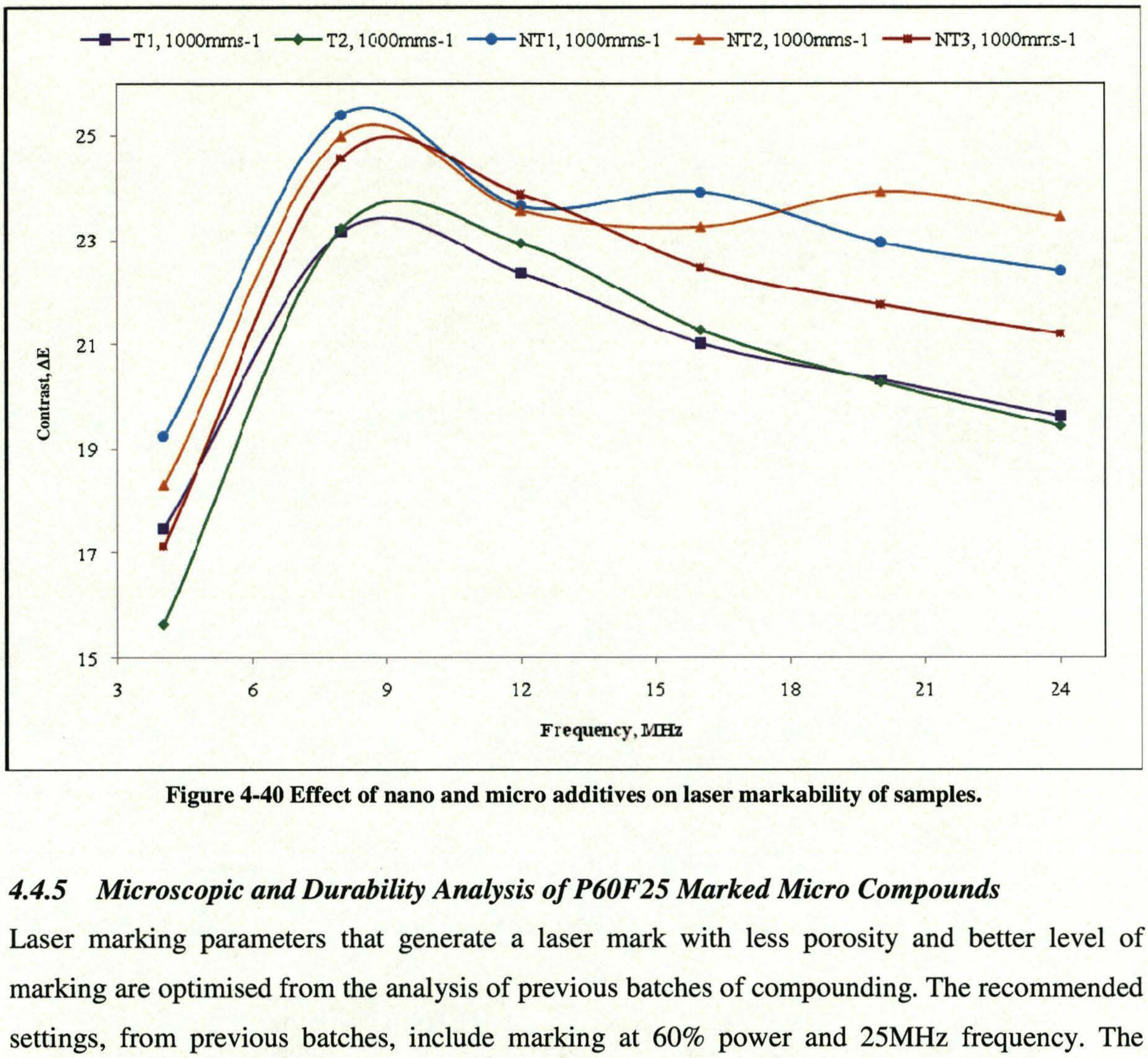


Figure 4-40 Effect of nano and micro additives on laser markability of samples.

4.4.5 Microscopic and Durability Analysis of P60F25 Marked Micro Compounds

Laser marking parameters that generate a laser mark with less porosity and better level of marking are optimised from the analysis of previous batches of compounding. The recommended settings, from previous batches, include marking at 60% power and 25MHz frequency. The micro-size additives used for compounding were also recommended from previous batches including A, T, B and S. Therefore, B and S are mixed in different combinations with A and T as shown in table 4.7, to study the subsequent effects of different additives individually and also in combination.

In accordance with one standard testing regime established for this project, the samples were subjected to a series of durability tests including the specialised wear testing, accelerated UV weathering and chemical resistance test over a period of 4 weeks. The samples were kept under

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NT1-NT3: 0.05-0.2% Nano TiO_2; NZ1-NZ3: 0.05-0.2% Nano ZnO; NC1-NC3: 0.05-0.2% Nano CuO
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

the UV light in the QUV weathering tester for 16 hours a day and the remaining 8 hrs in an industrial oven at 60°C immersed in two different sweat solutions (acidic and basic). The initial test plan involved carrying out the specialised wear test, as a part of the durability analysis, for 10 minutes per week, adding to 40 minutes (3000cycles) over a 4 week period. Samples are to be removed after every week for chromometry and microscopic analysis.

Preliminary results of the specialised wear test carried out separately rather than as a part of the durability analysis, showed that the laser marks were completely obliterated in the 1500-2000 cycle range. Therefore, the laser marks would be lost completely before the 4 week period which would not give any result for the durability analysis. This compelled the objective of undertaking the durability analysis without the specialised wear test.

Chromometry is carried out on the samples removed from the test setup after each of the 4 weeks of the test period to record the difference in contrast. Results of the BT sample are shown in figure 4.41 which indicate an inconsistent increase and decrease in the contrast value at each measurement. Linear trendlines are drawn which clearly show a decrease in the contrast over the four week period.

The line of best fit for a given set of data can be a straight line or a curve depending on various parameters. In the present case where the values (contrast, ΔE) are widely spread, linear trendlines are best fit in order to estimate the rate of decrease in contrast with time. The rate at which deterioration occurs on the laser marked area can be calculated and estimation of the time when complete loss of contrast would happen may also be calculated by extrapolating the data. From the figure 4.41 it can also be seen that wear of samples immersed in acidic sweat solutions is more than the samples in basic sweat solutions and this trend can also be seen in most of the remaining samples.

T1-T2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

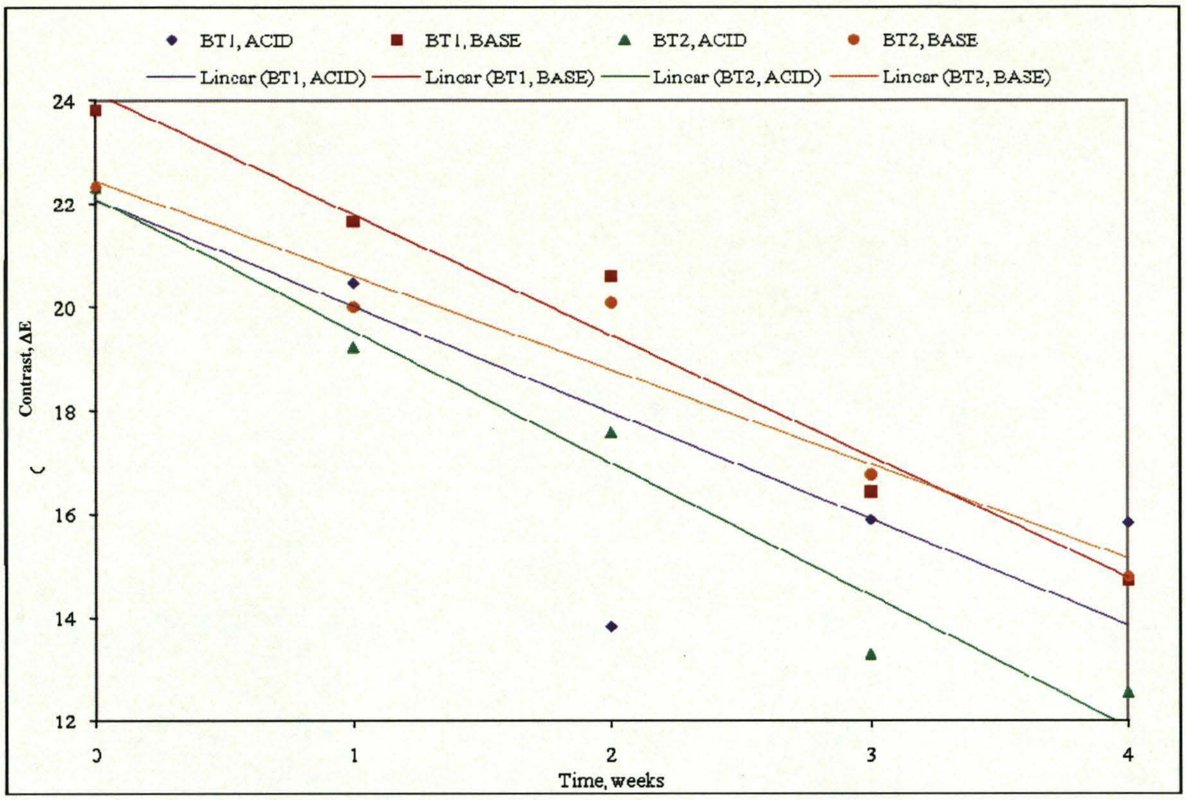

Figure 4-41 Affect of light and sweat on laser marked BT sample.

From figure 4.42, it can be seen that the porosity of the laser mark has drastically increased by the end of 4 week test period, and could be the primary reason for decrease in contrast values seen in figure 4.41. The wear behaviour of the contrast values, of most of the samples, during the 4 week testing period might be due to the deposition of salts during the test process. The extra salt on the surface made it uneven which assisted in reflecting the incident light successfully and resulted in greater contrast values, with even more deposition the salt might have washed away or fallen off due to increased weight and low bonding strengths resulted in lower contrast values. A close examination of the micrographs shown in figure 4.42 of SA2 samples immersed in acidic sweat solution reveals the deposition of salts after week 1. EDXA on the samples shows presence of elements such as sodium (Na) or chlorine (Cl) in the spectra, figure 4.43. These results corroborate the explanation that salt deposition might be the reason for inconsistency in contrast values.

BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

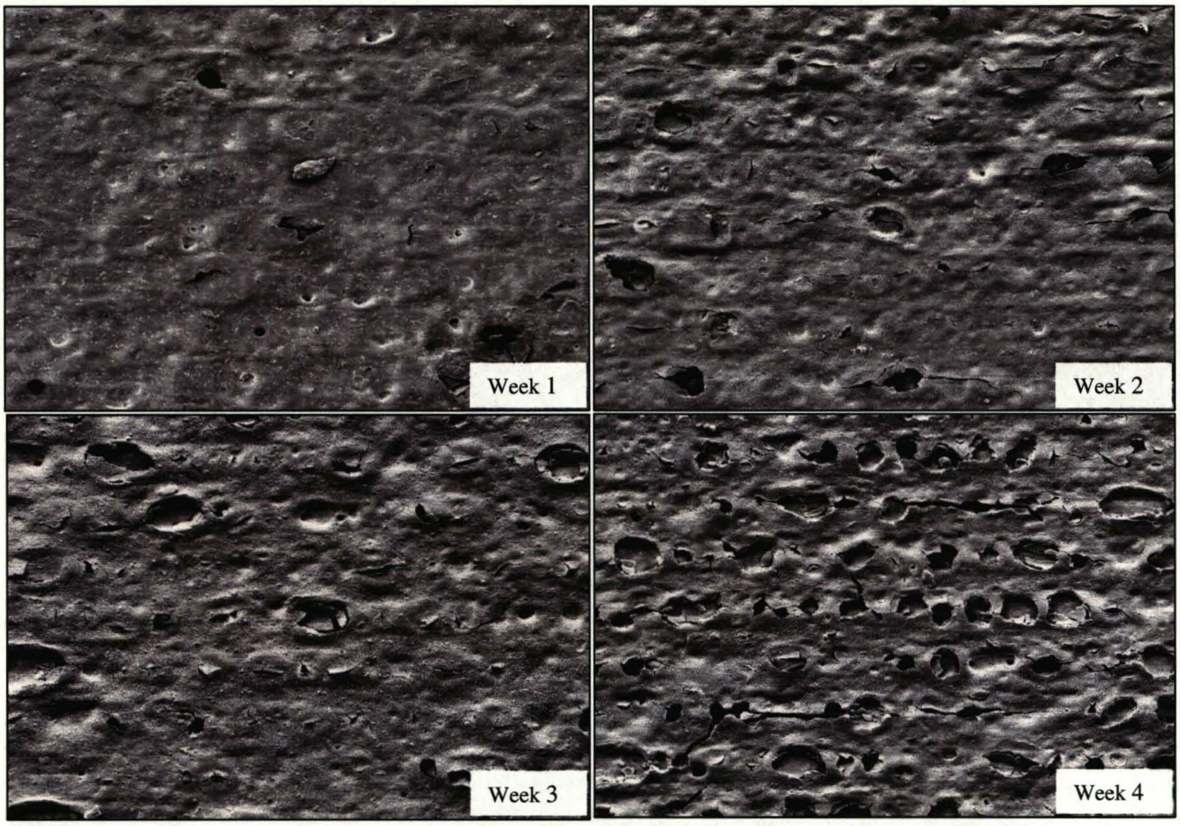

Figure 4-42 Micrographs of SA2 samples subjected to the unique test regime showing gradual deterioration after every week. 200X

Results of the remaining samples also show a similar trend and the graphs are included in the Appendix, for reference purposes (Section 8.3, page no.118-122). However, the rate at which wear of the laser mark occurred is different for different samples. Further, table 4.15 shows the contrast values of the all the micro compounds which are subjected to the 4 week durability test regime.

AO1-AO2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
TO1-TO2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

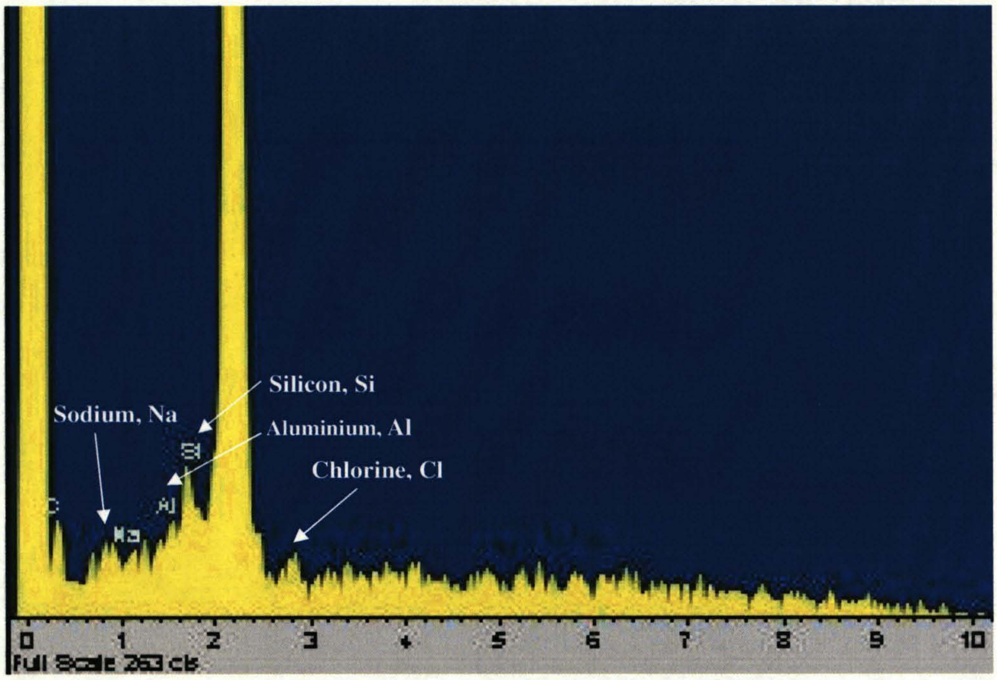

Figure 4-43 EDXA spectrum of SA2 showing the presence of Na and Cl after week 2 of the durability analysis.

	ACID					BASE			
	ORIGINAL	**WEEK1**	**WEEK2**	**WEEK3**	**WEEK4**	**WEEK1**	**WEEK2**	**WEEK3**	**WEEK4**
T1	19.22	20.03	18.55	15.09	**17.43**	**18.64**	20.42	19	18.7
T2	19.26	17.35	14.07	**16.32**	**17.14**	19.74	18.51	**15.61**	**16.72**
BT1	23.82	20.48	**13.84**	15.89	15.84	21.66	20.61	16.44	14.73
BT2	22.32	19.22	17.57	13.28	12.54	20	20.09	16.76	14.8
ST1	20.89	20.41	17.53	12.59	**14.48**	--	19.34	**17.3**	**17.52**
ST2	22.08	19.04	18.23	18.22	17.41	18.53	**16.4**	**19.17**	15.06
A1	21.97	19.61	15.9	13.84	12.66	21.73	20.24	16.36	13.61
A2	22.5	21.13	15.21	15.66	**19.35**	22.24	19.53	17.35	16.25
BA1	24.2	21.38	17.38	**21.23**	11.95	23.35	18.07	19.06	16.02
BA2	21.22	17.73	15.8	14.29	**18.6**	21.64	19.89	18.43	15.19
SA2	24.35	22.02	18.45	18.02	14.42	21.3	20.68	17.44	17.51
SA2	22.36	21.11	18.06	**15.76**	16.92	22.37	19.48	18.56	17.08

Table 4.15 Contrast values of the micro compounded samples after durability analysis.

AO1-AO2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
TO1-TO2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

Results from the wear test show that most of the micro compound samples marked at P60F25 setting only withstood 2000 cycles which indicates they failed the test. Samples were digitally photographed for future reference.

4.4.6 Microscopic and Durability Analysis of P60F25 Marked Nano Compounds

Nano additives such as NT, NZ and NC mixed with ABS at different weight percentages and marked at 60% power and 25MHz frequency setting (P60F25) are discussed in this section. The samples underwent a combination of durability tests, described earlier. Chromometry is carried out on the samples after every week to measure any difference in contrast. The contrast values in most cases show a wavy pattern from week to week, as explained in section 4.4.5. However, figure 4.44 shows the trendlines of NZ nano-compound illustrating that, although the contrast values are inconsistent, there is a decrease in the contrast over the 4 week period.

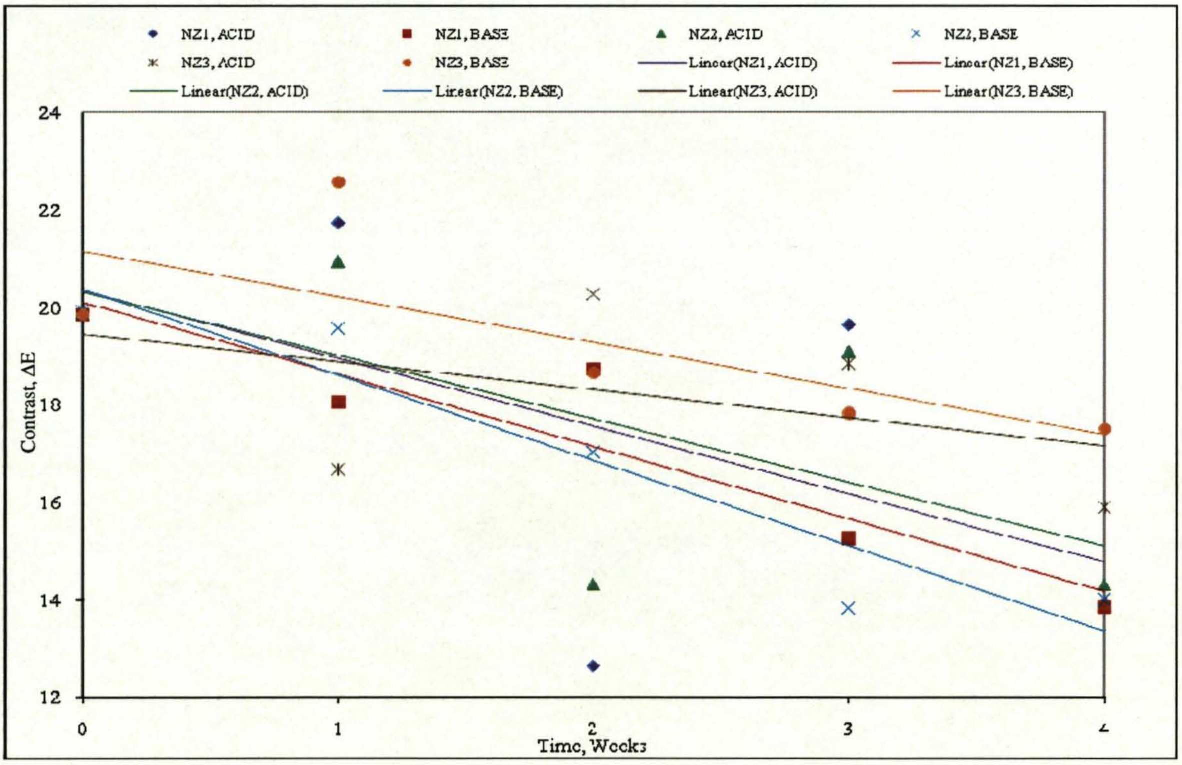

Figure 4-44 Contrast values of nano compounds after Durability tests.

NT1-NT3: 0.05-0.2% Nano TiO_2; NZ1-NZ3: 0.05-0.2% Nano ZnO; NC1-NC3: 0.05-0.2% Nano CuO
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

Figure 4.45 shows the deterioration of the NC3 samples immersed in acidic solution due to increase in porosity, as observed in SA2 sample shown before, which is a part of the 4 week unique test regime used to determine the durability of the laser marks. The micrographs show some deposition of salt which might be the reason for inconsistent contrast values. Figure 4.46 shows the EDXA spectra of NC3 compound which confirms the presence of sodium and chlorine on the surface of the sample.

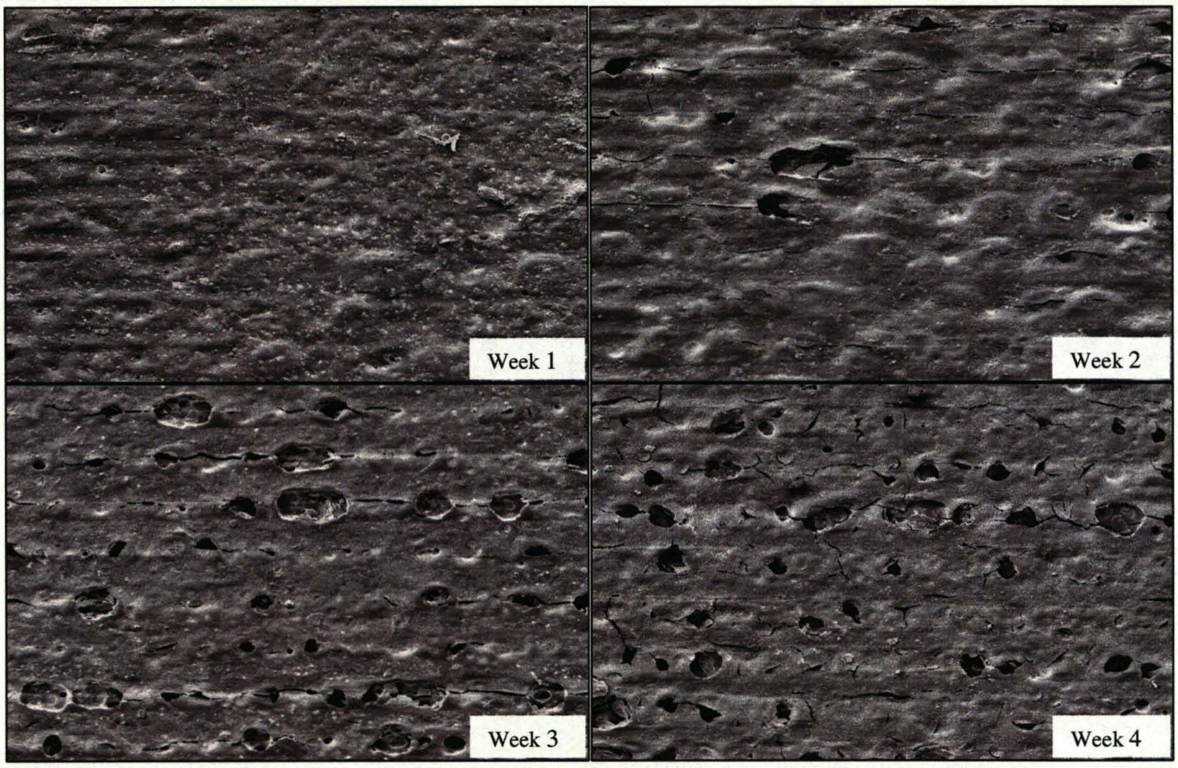

Figure 4-45 Micrographs of NC3 samples subjected to the unique test regime showing gradual deterioration after every week. 200X

NT1-NT3: 0.05-0.2% Nano TiO_2; NZ1-NZ3: 0.05-0.2% Nano ZnO; NC1-NC3: 0.05-0.2% Nano CuO
AO1-AO2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
TO1-TO2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

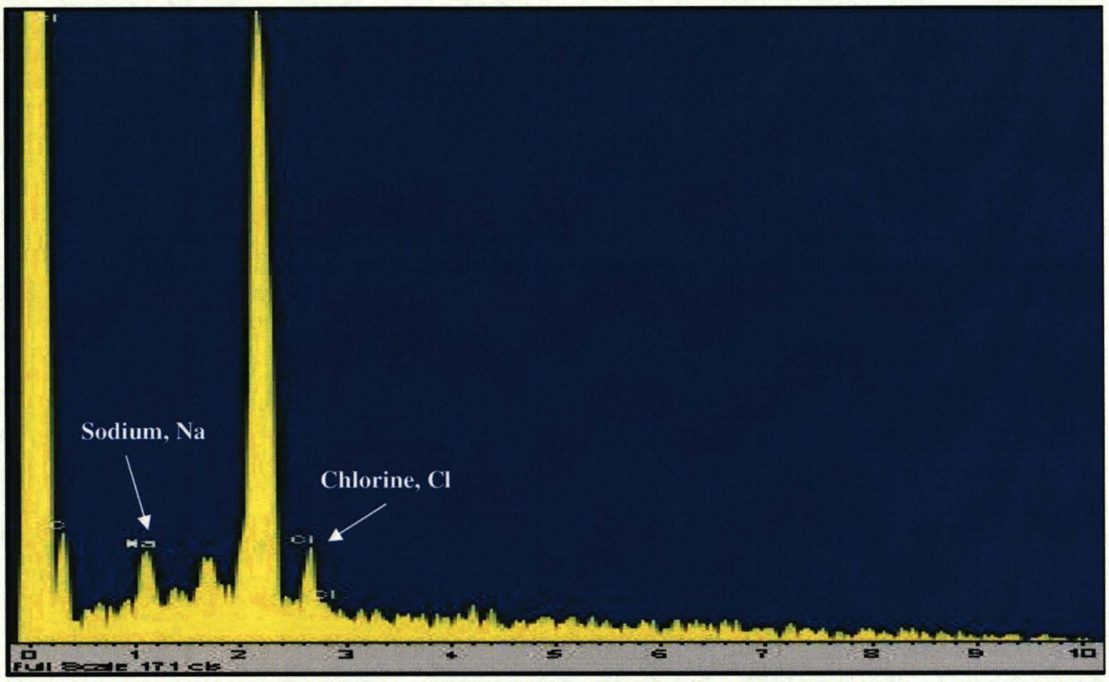

Figure 4-46 EDXA spectrum of NC3 compound showing the presence of Na and Cl after week 2 of the durability analysis.

NT1-NT3: 0.05-0.2% Nano TiO_2; NZ1-NZ3: 0.05-0.2% Nano ZnO; NC1-NC3: 0.05-0.2% Nano CuO
AO1-AO2: 0.6-1.0% Al_2O_3; BA1-BA2: 0.3-0.6% Bone Char + 0.6% Al_2O_3; SA1-SA2: 0.3-0.6% Silicon + 0.6% Al_2O_3
TO1-TO2: 0.6-1.0% TiO_2; BT1-BT2: 0.3-0.6% Bone Char + 0.6% TiO_2; ST1-ST2: 0.3-0.6% Silicon + 0.6% TiO_2
1A-1E: 250mms^{-1} Speed, 4-24MHz Frequency, 60% Power; 2A-2E: 1000mms^{-1} Speed, 4-24MHz Frequency, 60% Power

5.0 CONCLUSIONS AND FUTURE WORK

The first objective of this project was to investigate the reasons for the lack of initial contrast and subsequent durability of light coloured laser marks on dark coloured plastics materials used in commercially available computer keyboards. A more fundamental understanding of the laser-material interaction during the marking process was then developed, which in turn enabled the formulation of selected plastics materials to be adapted and laser settings to be optimised for improved levels of character contrast and durability.

Materials development involved employing various additives in the base ABS polymer which was combined with an extensive investigation into the effects of changing the laser settings used during marking. The substantial amount of test data and associated micrographs generated by this experimental process, were subsequently analysed and interpreted. The following major conclusions can be drawn:

1. Morphological analysis of the commercially available laser marked keycaps was undertaken to understand the laser-material interaction, using a scanning electron microscope. This showed that the characters were generated by a foaming mechanism, where some marks were smooth (closed cell foam pattern) and others exhibited a much rougher appearance (open cell foam pattern). The absence of an open cell foam pattern, which reflects incident light diffusively, is believed to be the reason for lack of initial contrast of a light coloured laser mark on the underlying dark coloured background. Further, the foamed surface was worn away during service due to impact caused by the fingers while typing and resulted in discolouration of the character in less than 6 months.

2. Literature review suggested that matching the absorption wavelength of an additive to that of the wavelength of the laser light (Section 2.7 and Figure 2.14), is the main criterion for selecting a laser sensitive material and typically, the greater the laser sensitivity the higher the initial contrast of the laser mark. However, evidence from the work based on aluminium trihydroxide and titanium dioxide (with absorption wavelengths of 388 nm & 386-413 nm respectively) have shown this approach is too simplistic and clearly other factors such as

specific heat, formulation of the compound clearly have a major effect on the initial contrast, when marked with a 1064 nm Nd:YAG laser.

3. Aluminium trihydroxide generated laser marks with higher contrast ($\Delta E^*=24.76$) and showed improved durability performance (1500-2000 wear cycles to complete removal of the laser mark) when compared with all the other additives used in this work.

4. Nano-additives such as nano titanium dioxide performed better when compared to micro-additives such as titanium dioxide in terms of contrast ($\Delta E^*=25.4$) and durability performance (1500-2000 wear cycles to complete removal of the laser mark).

5. The plaques that were laser marked with a specially designed grid pattern, involving changes to the laser light frequency and the speed of laser marking, provided an extensive and comprehensive data set. This enabled the laser marking settings to be optimised so that for a specific mix of base polymer and additive, the best combination of character contrast and durability could be achieved. The evidence from the present work indicates that the optimum settings for an Nd-YAG laser are a frequency of 8MHz and a marking speed of 1000 mms^{-1}. Surprisingly this applied to all the additives used during the project. However, it is recommended that the laser parameters should be optimised for each base polymer and additive system used.

6. A unique durability test regime has been designed to measure the life expectancy of laser marks which combined the effects of impact, sweat and light. The test includes 10 minutes per week of specialised wear testing combined with accelerated chemical resistance test and accelerated ultra-violet weathering test for 8 and 16 hours per day respectively. Results from the test indicate a definite loss of the laser marked character with time. The unique testing regime applied to the samples proved to be an appropriate simulation of the environmental effects to which computer keyboards are subject in practice.

* ΔE is the difference in contrast between the laser mark and the underlying dark base material.

5.1 Future Work

The current work can be developed by investigating a new range of additives to study and understand the laser sensitivity of plastics materials. For example, the combination of aluminium trihydroxide, which demonstrated superior contrast and durability characteristics in the present research, and other base materials such as PC, PC-ABS blends etc., should be investigated. Furthermore, there appears to be significant potential, for laser marking purposes at least, in the use of nano-additives and in particular, nano aluminium trihydroxide.

Use of a diode-pumped Nd:YAG laser will allow the plaques to be laser marked in a grid-like pattern with Power and frequency on the x & y axis respectively which would increase the scope of work. Also, use of a 532nm Nd:YAG green laser would actually affect the additives the in the compound to generate a laser mark through colour change mechanism. Further, the unique test regime designed to study the durability of the keycaps could be carried out to estimate the life of the mark. Building a customised wear test rig by amalgamating the UV weathering test, chemical resistance test and the wear test could also be considered. Finally, results from the laser marking and durability tests could be easily and effectively used to optimise the settings for different formulations in order to generate a character with the best combination of contrast and durability.

Employing the Design of Experiments (DoE) module to model the experiments might help in producing quality results with less number of experiments. Also, subjecting the samples through Atomic Force Microscope (AFM) would provide results with better information, such as images of the surface topography with atomic resolution. Talysurf could also be used to provide information about the surface roughness caused by the laser-material interaction.

Finally, it has been noted that there is a significant lack of research information available in the field of laser-material interaction. Although, it is understood that this field can often be subject to commercial sensitivities, an improved understanding of the laser marking of plastics and its applications will only be achieved if research is disseminated within the public domain.

6.0 REFERENCES

1. Meruva, S., *Quality and Durability of Characters on Computer Keycaps*, in *School of Engineering*. 2003, Napier University: Edinburgh.

2. Campbell, A. M., *Visual Aids for Keyboard Printing Processes*. 2002, NMB Minebea UK Ltd.: Glasgow.

3. *Laser Marking Technologies 2002*, www.sintecoptronics.com visited in September 2004, Sintec Optronics Pte. Ltd.: Singapore.

4. *Laser Marking Technology - White Paper*, www.advanced-input.com visited in January 2004, Easterline, Advanced Input Systems: USA.

5. Mulholland, B.M., *A Report on Laser Markable Engineering Resins*, www.ticona.com visited in March 2004, Ticona, USA.

6. *Technical Information on Laser Marking* 2001, www.trumpf.com visited in November 2005, TRUMPF Laser Marking Systems AG, Germany.

7. *Laser Marking on Plastics Materials,* www.rofin-basel.com visited in January 2004, Rofin-Basel, USA.

8. Sabreen, S.R., *New Technologies of High Speed Colour Laser Marking of Plastics*, in *Plastics Decorating Magazine* 2005, Peterson Publications.

9. Hecht, J., *Laser Guidebook*. 2nd ed. 1992: McGraw-Hill Publications Inc., Page no. 20-57 & 389-417.

10. *Laser Marking Centre,* www.specialchem4polymers.com visited in January 2004, SpecialChem Knowledge and Solution Provider.

11. Graff, G., *Laser Marking makes Bigger Imprint in Plastics* visited in January 2004, www.omnexus.com, Omnexus.

12. Hoffmann, P., *Micro-usinage Laser, STI, Microtechnique, Ecole Polytechnique Federale De Lausanne, France.*

13. Amemiya, S. (2004) *Titanium-Oxide Photocatalyst,* Three Bond Technical News Issued in January 2004, Three Bond Company Ltd., Japan.

14. Zheng, H., *Laser-effected Darkening in TPEs with TiO_2 Additives,* Singapore Institute of Manufacturing Technology, Singapore. Article available from www.sciencedirect.com, Science Direct, June 2003.

15. Mustafina, V.N.K.a.N.T., *A study of the optical absorption induced in vacuum thermolysis of aluminium trihydroxide* Journal of Applied Spectroscopy, May, 1998. Volume 65(3): p. 5.

16. Chun-Liu Fang, K.Q., Jianhua Zhu, Shangbin Wang, Xiaoxuan Lv and Shu-Hong Yu, *Monodisperse α-Fe2O3@SiO2@Au core/shell nano-composite spheres: synthesis, characterization and properties.* IOP, Electronic Journal (Nano Technology), 2007: p. 7.

17. Bryson, J.A., *Plastic Materials.* 4th ed. 1999: Butterworth Scientific publication, page no.119-150.

18. James B Carroll Jr. and Steven A Jones, Patent on *Additive for YAG Laser Marking* 2004 (Patent No. US 6693657 B2) , Engelhard Corporation, NJ (USA): USA.

19. Kniess Helge, Dieter Heinz, Reiner Delp, Gerrard Pfeff and Matthias Kuntf, Patent on *Laser-Markable Plastics.* 2004 (Patent no. US 6727308 B2), Merck Patent Gesellschaft mit beschrankter Haftung: Germany.

20. Jae Hong Choi, Patent on *Laser Markable ABS polymer for Telecommunications Terminals and Keypads.* 1999 (Patent no. 5981640), Lucent Technologies Inc., NJ (US): USA.

21. Rein M Faber, Theodorus L Hoeks and Andre Volkers, Patent on *Copper Salts for Laser Marking of Thermoplastic Compositions.* 1996 (Patent no. 5489639), General Electric Company: Netherlands.

22. George E Sakoske and Joseph E Sarver, Patent on *Bismuth-Containing Laser Markable Compositions and Methods of making and using the same.* 2004 (Patent no. US 6680121 B2), Degussa Metals Catalysts Cerdec AG: Frankfurt.

23. Tammy E Link, Mark J Tellefsen and Shane F Drener, Patent on *Laser-Markable Plastics.* 2004 (Patent no. 7169471), EMD Chemical Inc.: USA.

24. James B Carroll Jr. and Steven A Jones, Patent on *Nanometer Size Antimony Tin Oxide (ATO) particles Comprising Laser Marking Additive.* 2004 (Patent Application no. EP20040800763), Engelhard Corporation: USA.

25. Rainer Linzmeier, Burkhand Krietsch and Frank Prissok, Patent on *Laser-Markable Plastics.* 2003 (Patent no. US6521688 B1), Merck Patent Gesellschaft mit beschrankter Haftung: Germany.

26. Hiroshi Sagane, Shinichiro Imanishi and Katsuhiko Sumida, Patent on *Resin Composition for White Marking.* 2002 (Patent no. US66420449 B1), Daicel Chemical Industries Ltd., Osaka: Japan.

27. *Knowing Colours*, Handbook for Minolta Chroma Meter, Published by Minolta, Page no. 1-20.

28. *Operating Manual* for QUV Accelerated Weathering Tester, Q Panel Company, Published by Q Panel Company, USA.

29. Oestreich, D.S., *UV Curable Silicones available from* 2001, Published by Degussa AG Goldshmidt Industrial Specialities, Germany.

30. UVPL-4019, D., *Clear UV Cure Coating Technical Data Sheet*, www.thermoclad.com, Published by Thermoclad, USA.

31. AS Edelstein, RC Cammarata and AE Edelstein, *Nano-materials: Synthesis, Properties and Applications* 1998, CRC Press and Publications, ISBN 07500739.

32. Scott R Sabreen, Special focus on *Decorating Plastics(Part 1-4)* 2004, www.sabreen.com, The Sabreen Group, Inc., USA.

7.0 BIBLIOGRAPHY

1. The Expanded Reach of Laser Marking, www.assemblymag.com visited in January 2004, AssemblyMag.

2. Durand, G., Microscopical and Durability Analysis of Laser-marked Polymer Nanocomposites. 2007, Napier University: Edinburgh.

3. Information on Calcium Stearate, www.greatvistahemicals.com visited in January 2005, Great Vista.

4. Hart, T., Information on Conductive/Magnetic Particulates, www.hartcoating.com visited in January 2005, Hart Coatings.

5. Merck, Lazerflair. 2006, Merck Ltd. (Pigment Division).

6. Meruva, S., Laser Markable Polymers. 2004, Napier University: Edinburgh.

7. Meruva, S. Laser Writable Polymers: Markability and Durability Characteristics. in Annual Technical Conference (ANTEC 2007). 2006. Cincinnati, USA.

8. Minelco Material Selection Sheets, www.minelco.com visited in January 2005, Minelco.

9. Sherman, L.M., Laser Marking has a Bright Future in Plastics. 2001, Plastics Online.

10. Siegbert Stober, U.K., Laser-Markable Thermoplastic Compounds, Degussa.

11. UVPL-4019, D., Clear UV Cure Coating Technical Data Sheet, Thermoclad.

8.0 APPENDICES

8.1 Appendix I (Batch I Formulations)

Micrographs of various additives used in batch I formulations which were marked at different power and frequency settings.

Figure 8.1.1 Micrograph sheet of Aluminium trihydroxide (A).

Figure 8.1.2 Micrograph sheet of Azodicarbonamide (AZ).

Figure 8.1.3 Micrograph sheet of Iron Oxide (F).

Figure 8.1.4 Micrograph sheet of Silver Coated Glass (SG).

Figure 8.1.5 Micrograph sheet of Phlogopite Mica (MP).

Figure 8.1.6 Micrograph sheet of Muscovite Mica (MM).

Figure 8.1.7 Micrograph sheet of Micafil-Vermiculite (MV).

Figure 8.1.8 Micrograph sheet of Iriodin (IR).

8.2 Appendix II (Batch II Formulations)

Micrographs of various additives and additive combinations used in batch II formulations which were marked at different power and frequency settings.

Figure 8.2.1 Micrograph sheet of Bone Char (B).

Figure 8.2.2 Micrograph sheet of Silicon (S).

Figure 8.2.3 Micrograph sheet of Aluminium trihydroxide + Iron Oxide (AF).

Figure 8.2.4 Micrograph sheet of Aluminium trihydroxide + Titanium dioxide (AT).

8.3 Appendix III (Batch III Formulations)

Graphs showing the results from the unique durability test regime for the batch III formulations marked at P60F25 laser marking setting.

Figure 8.3.1 Durability test results for Titanium dioxide (T).

Figure 8.3.2 Durability test results for Titanium dioxide + Silicon (ST).

Figure 8.3.3 Durability test results for Aluminium trihydroxide (A).

Figure 8.3.4 Durability test results for Aluminium trihydroxide + Bone Char (BA).

Figure 8.3.5 Durability test results for Aluminium trihydroxide + Silicon (SA).

8.1 Appendix-I (Batch I Formulations)

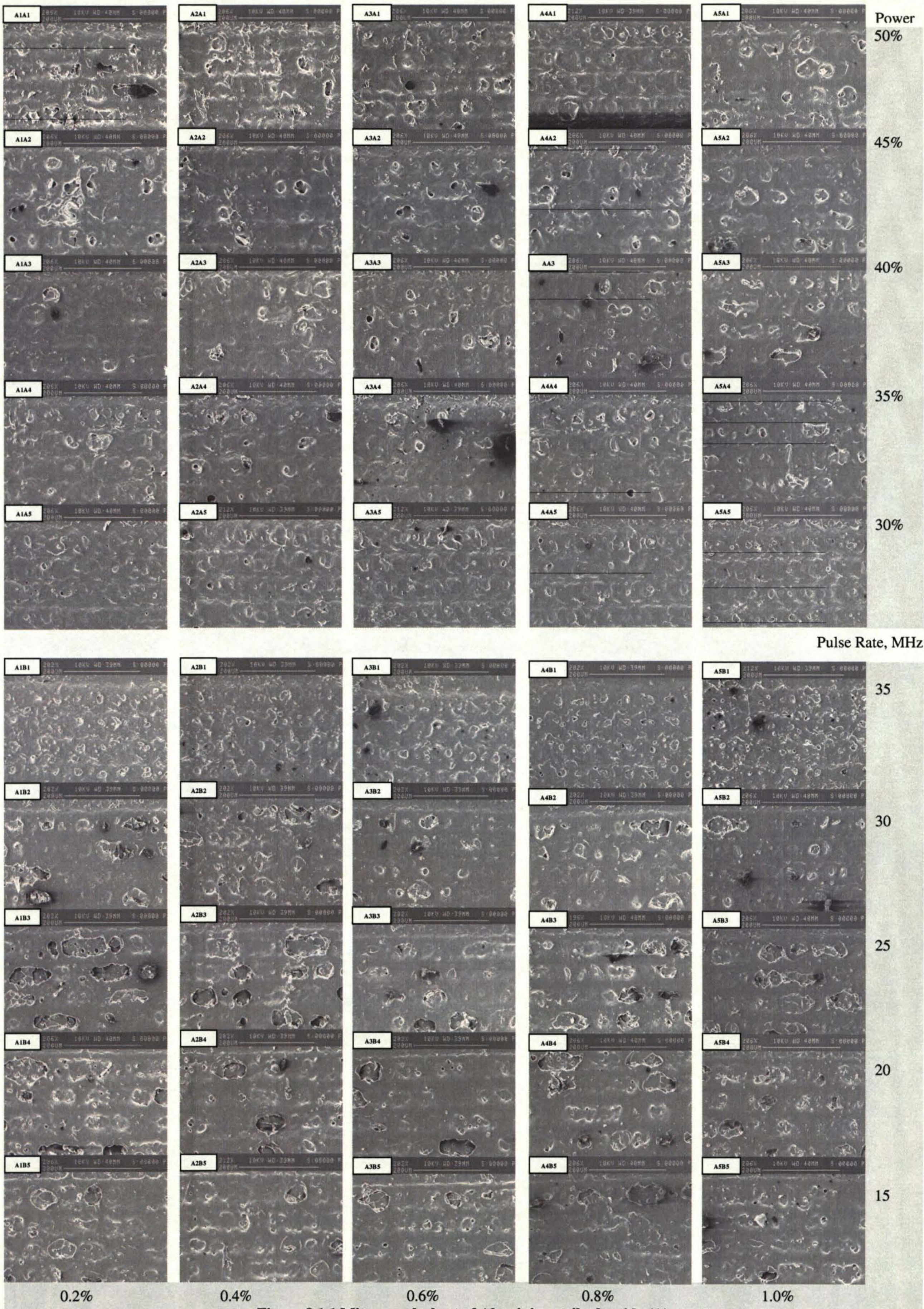

Figure 8.1.1 Micrograph sheet of Aluminium trihydroxide (A)

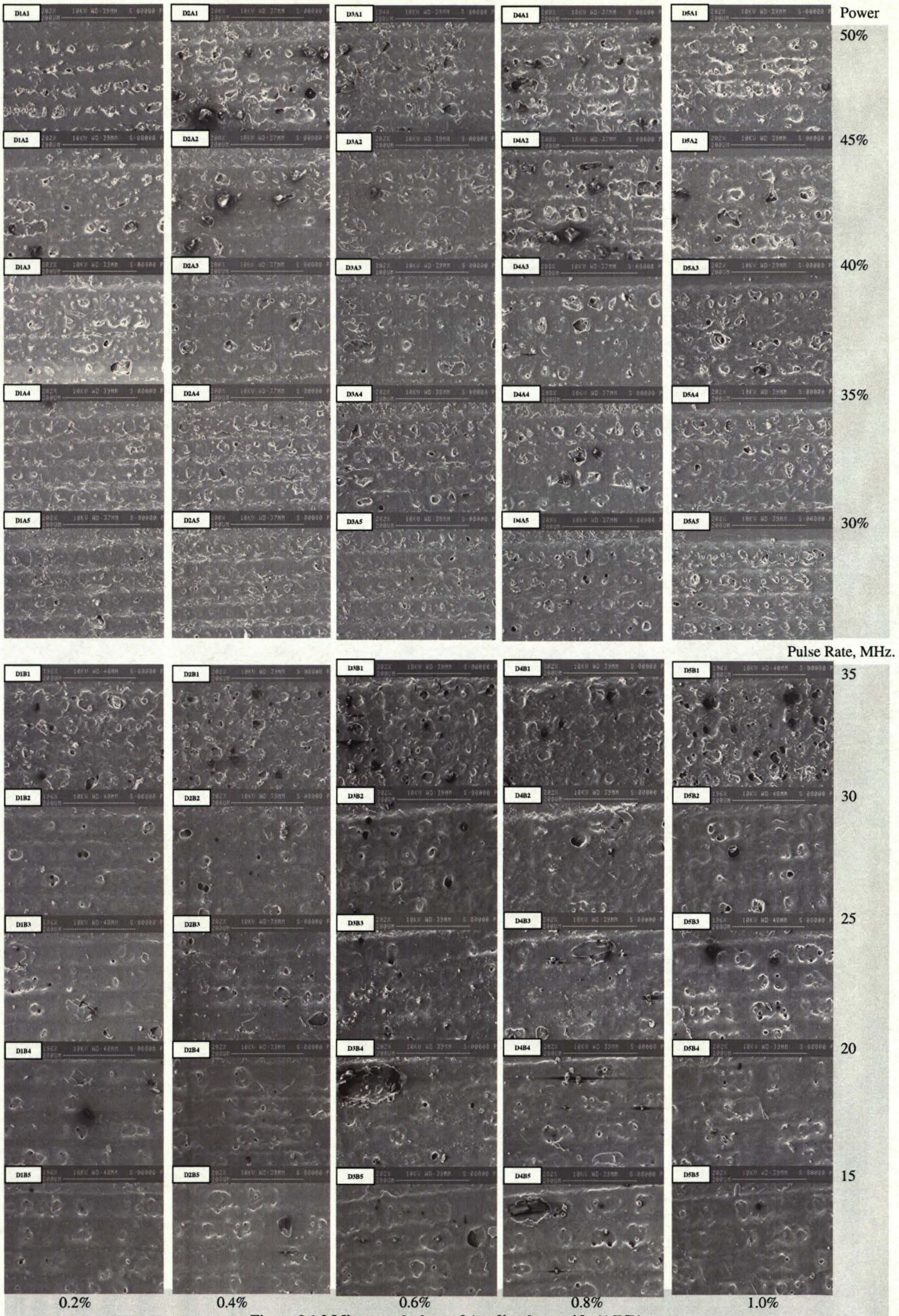

Figure 8.1.2 Micrograph sheet of Azodicarbonamide (AZ/D)

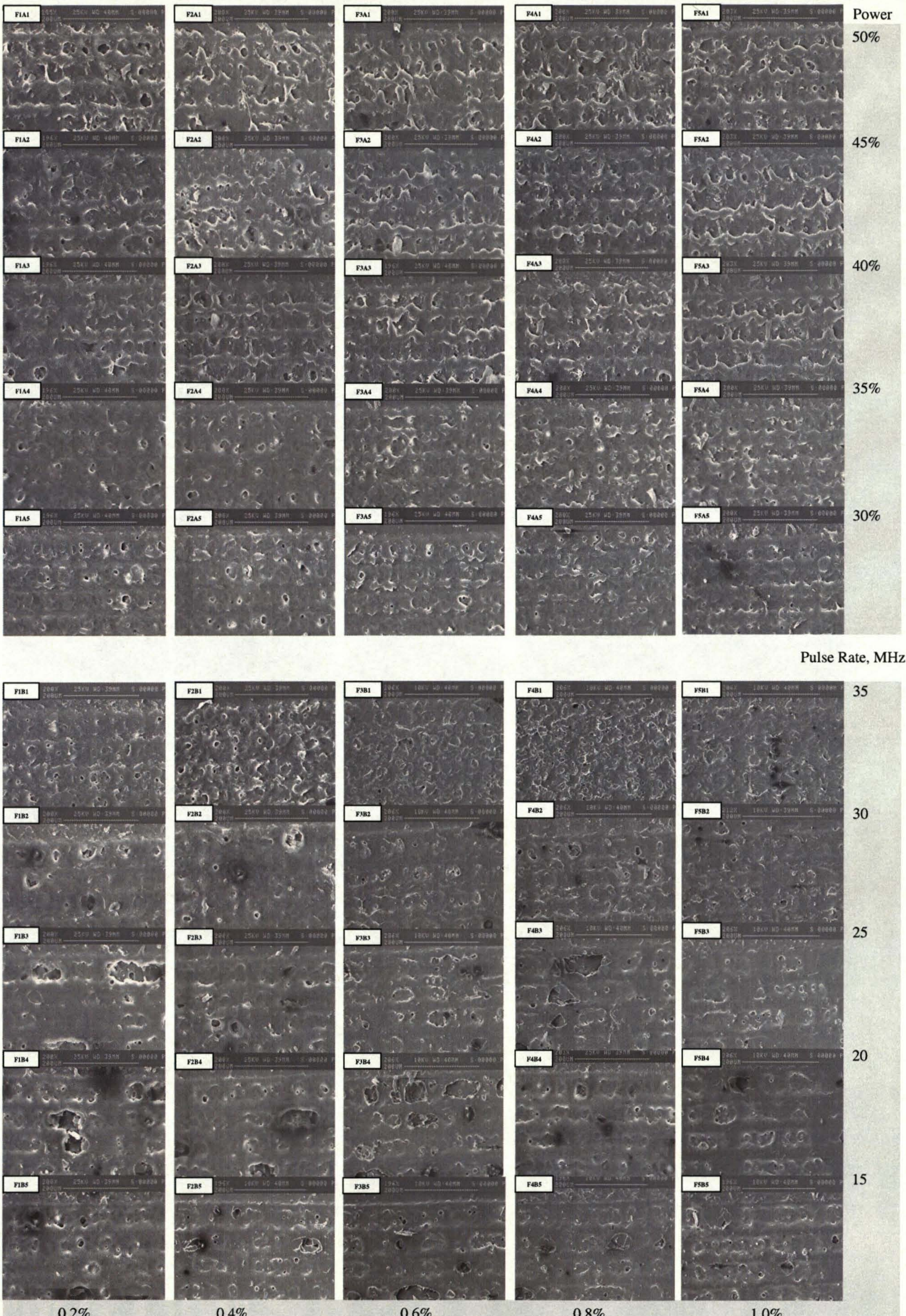

Figure 8.1.3 Micrograph sheet of Iron Oxide (F)

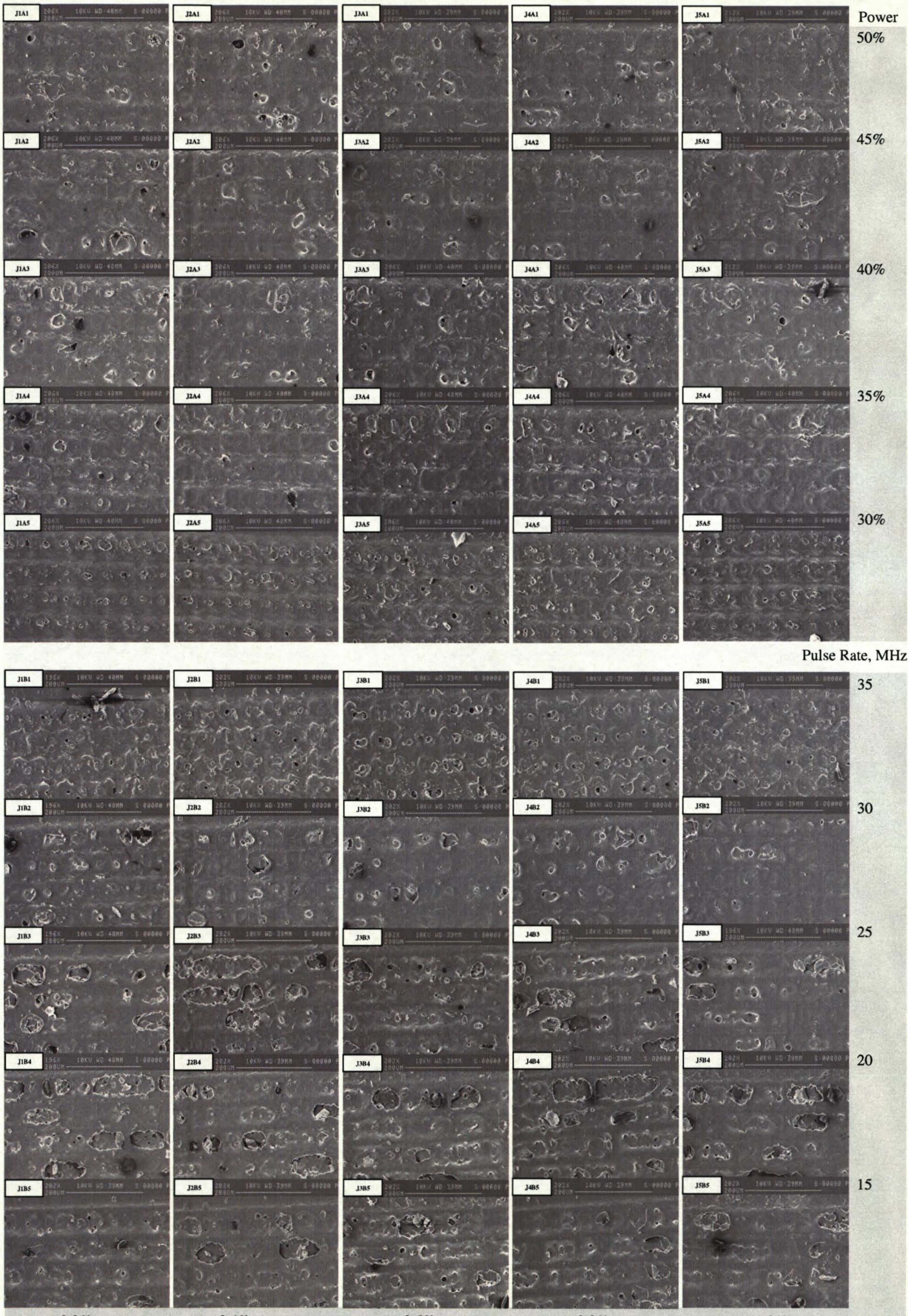

Figure 8.1.5 Micrograph sheet of Phlogopite Mica (MP/J)

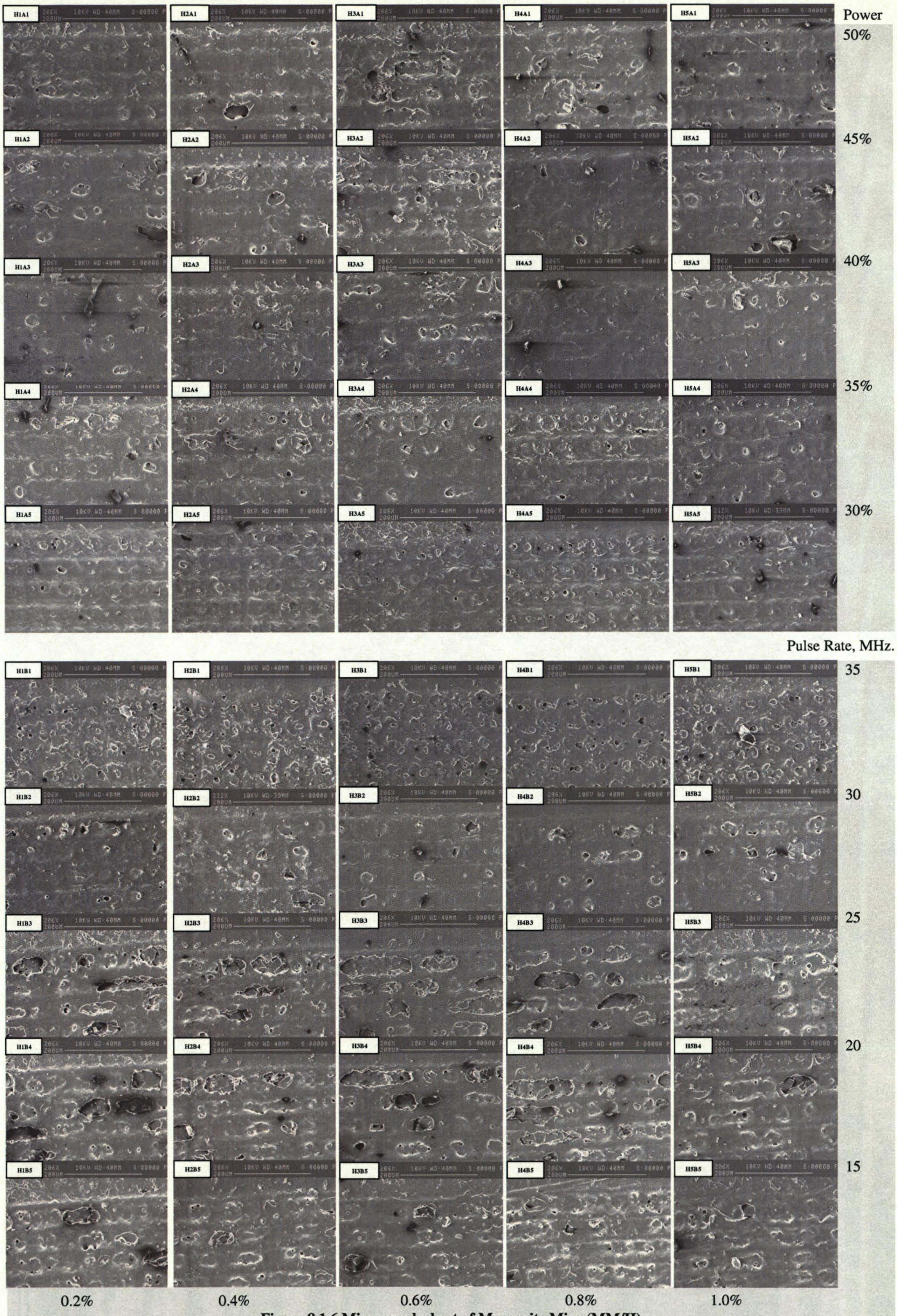

Figure 8.1.6 Micrograph sheet of Muscovite Mica (MM/H)

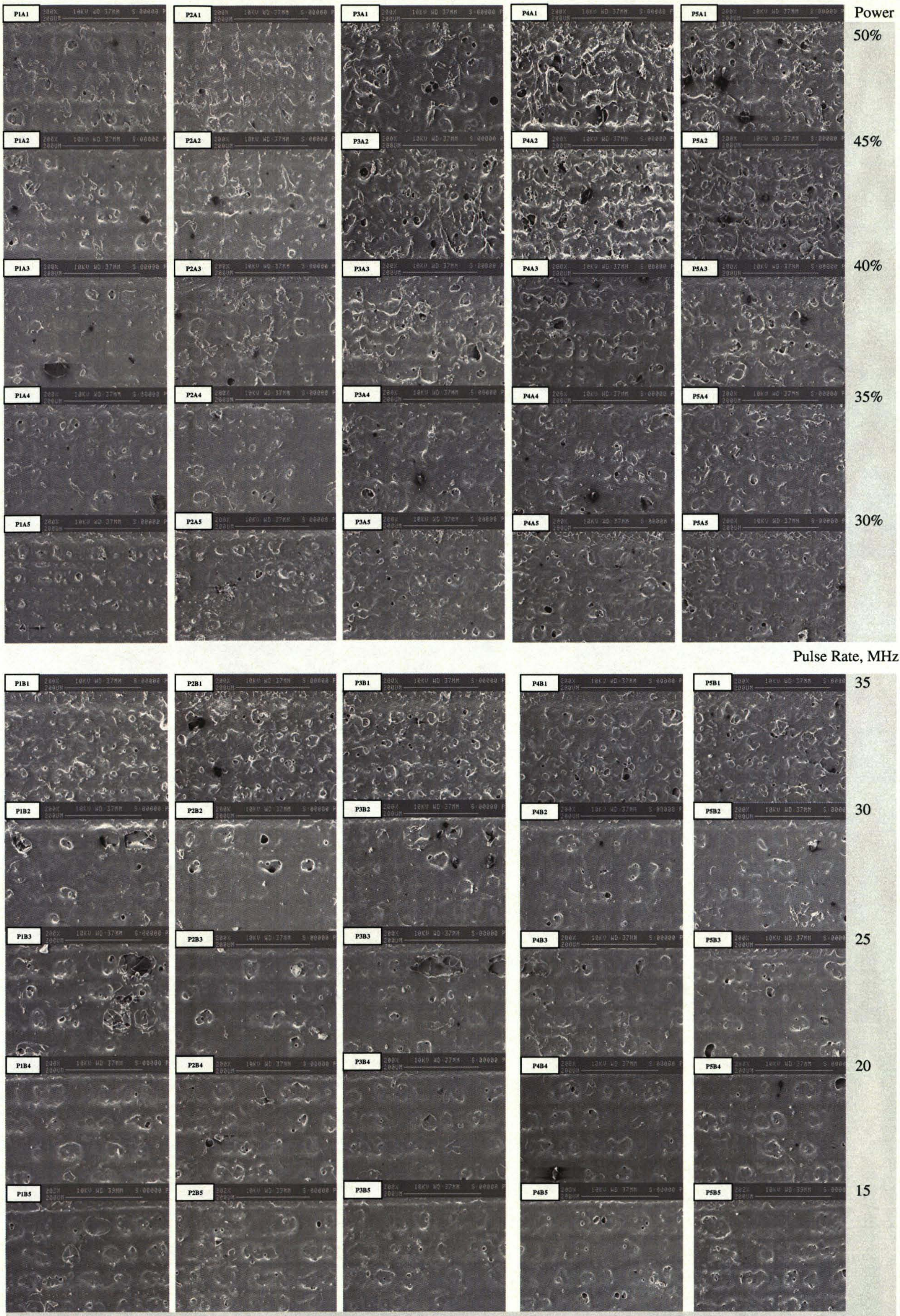

Figure 8.1.8 Micrograph sheet of Iriodin-Merck Compound (IR/P)

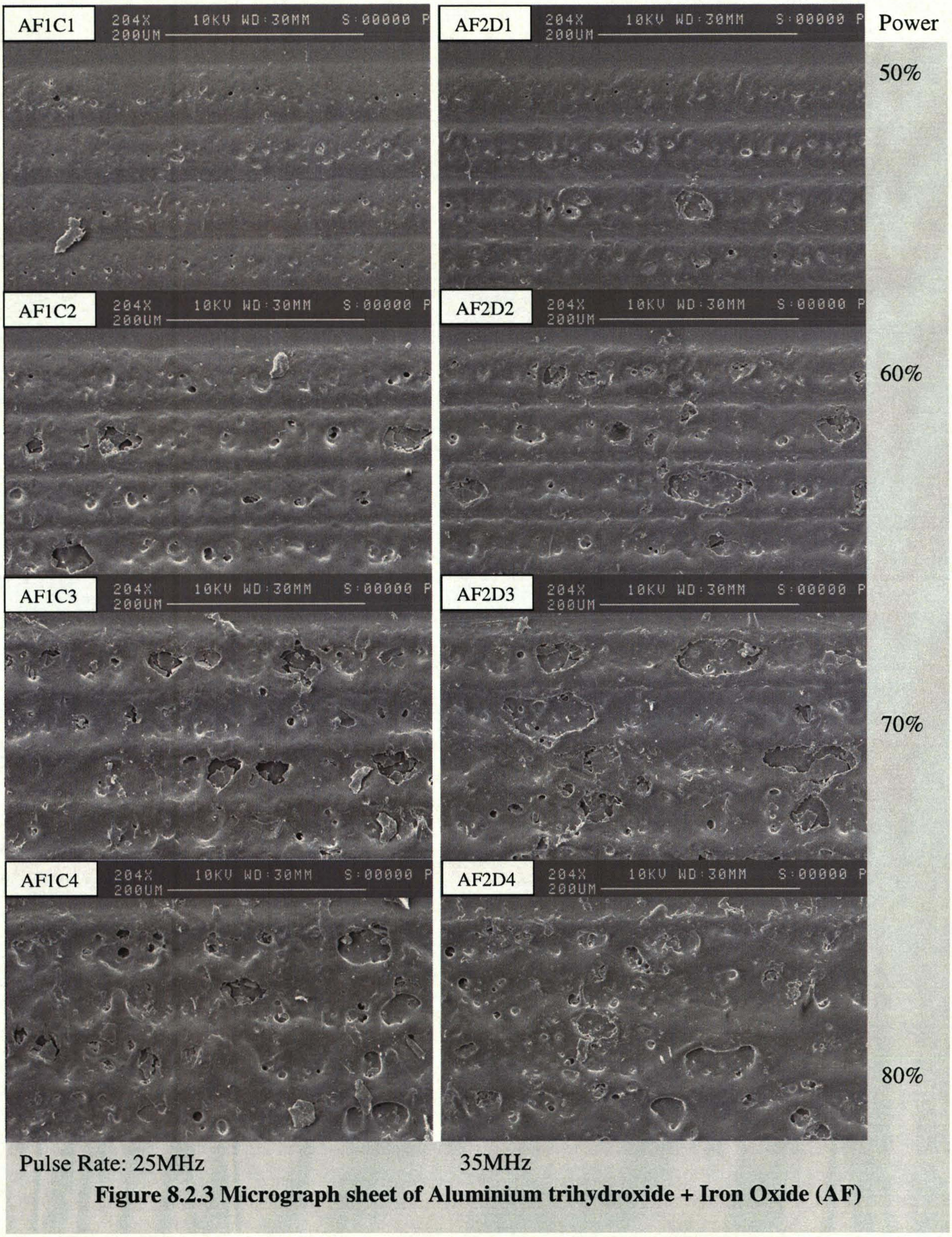

Figure 8.2.3 Micrograph sheet of Aluminium trihydroxide + Iron Oxide (AF)

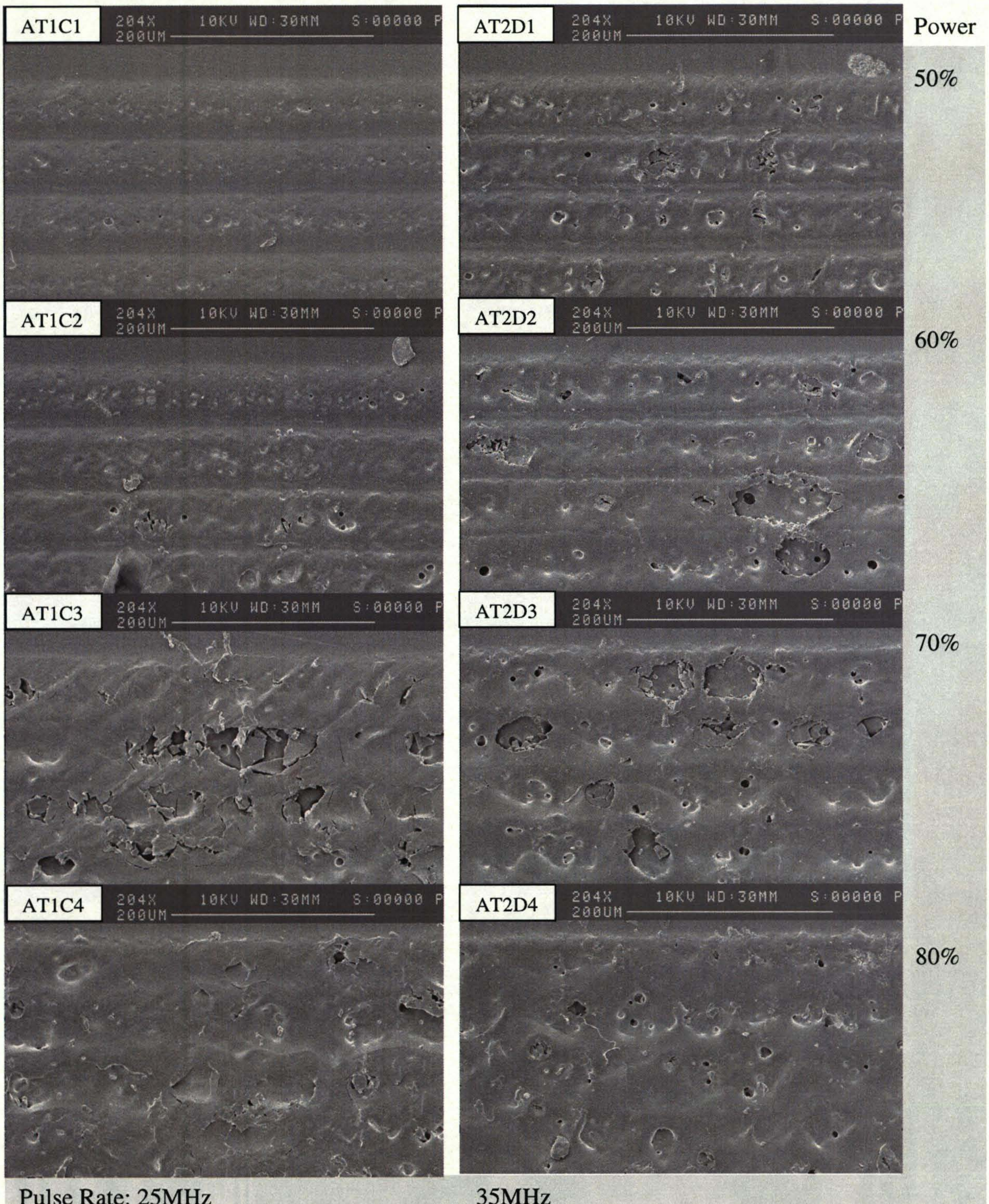

Figure 8.2.4 Micrograph sheet of Aluminium trihydroxide + Titanium dioxide (AT)

8.3 Appendix-III (Batch III Formulations)

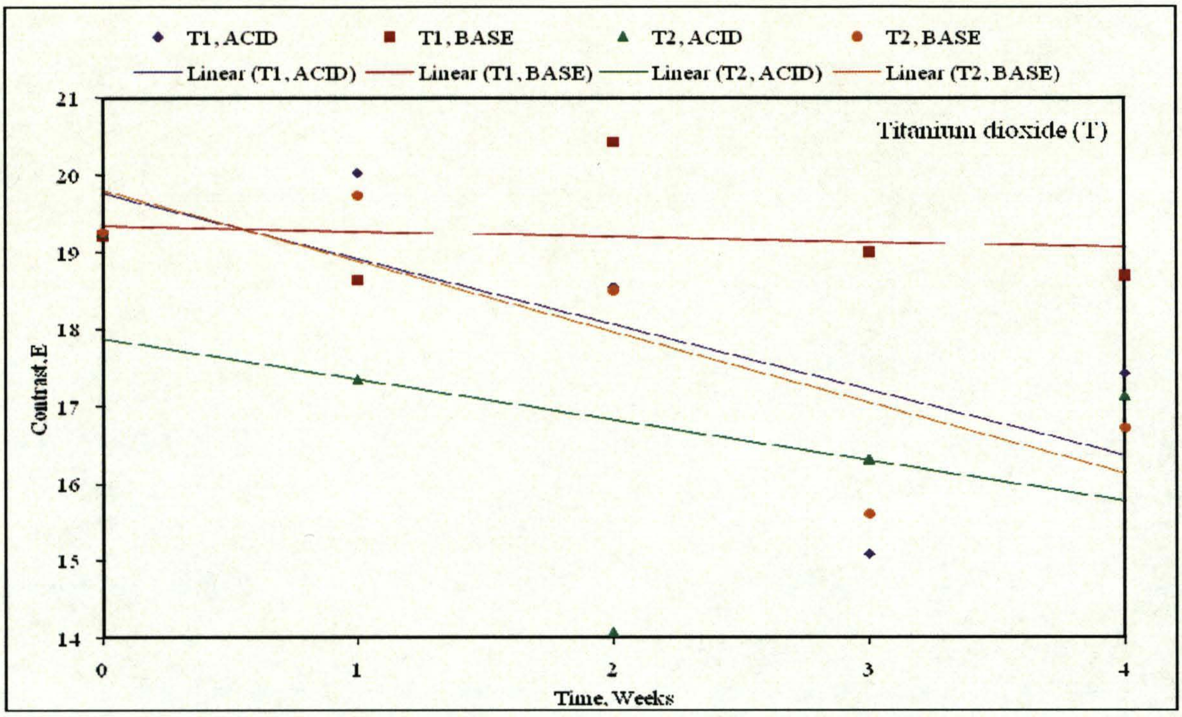

Figure 8.3.1 Durability Analysis results for Titanium dioxide (T).

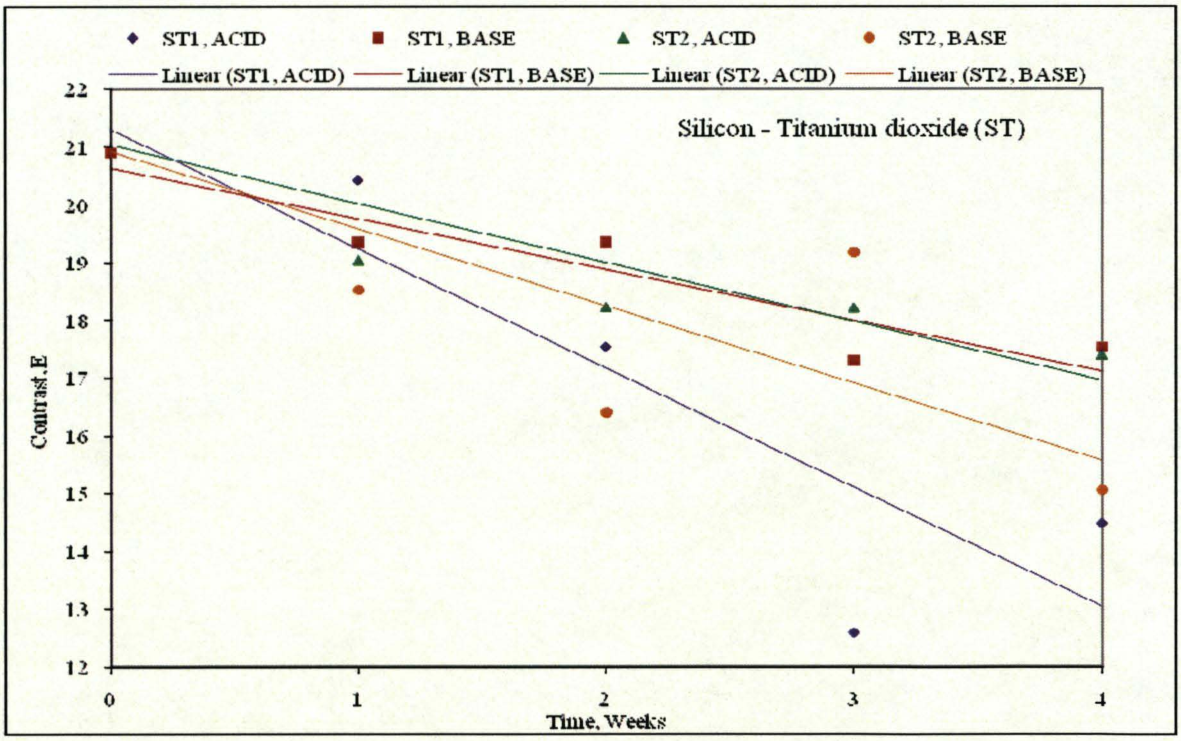

Figure 8.3.2 Durability Analysis results for Silicon + Titanium dioxide (ST).

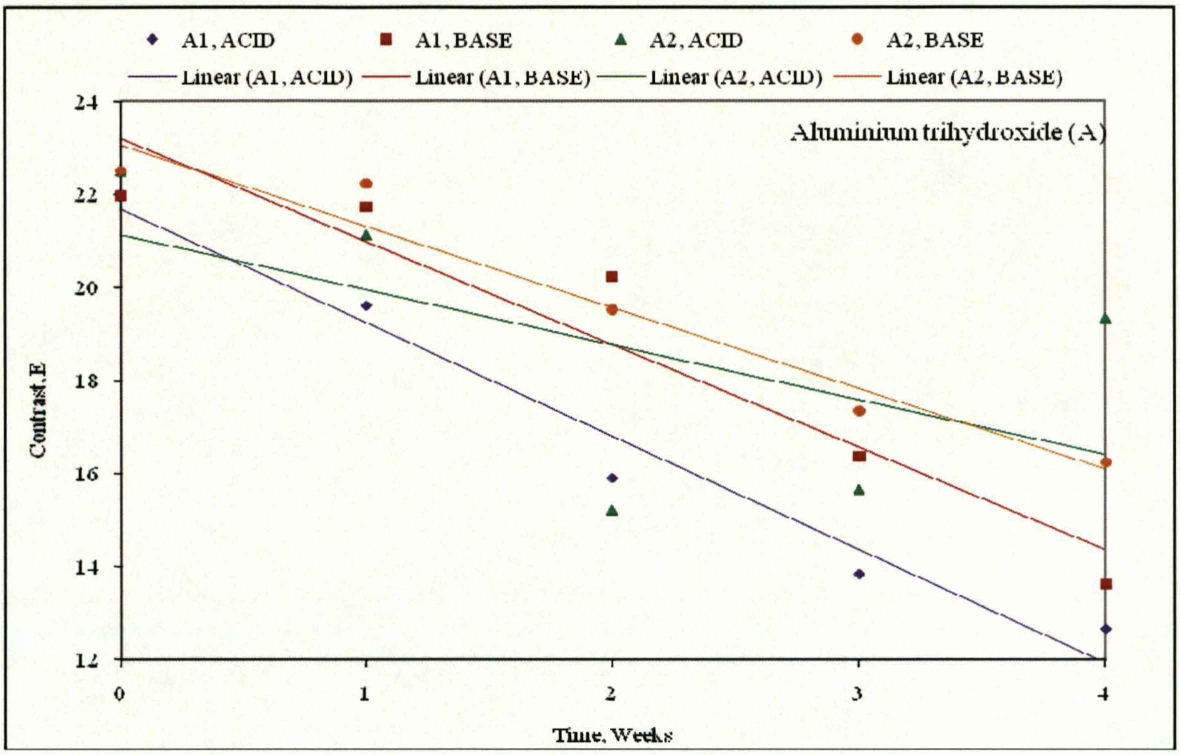

Figure 8.3.3 Durability Analysis results for Aluminium trihydroxide (A).

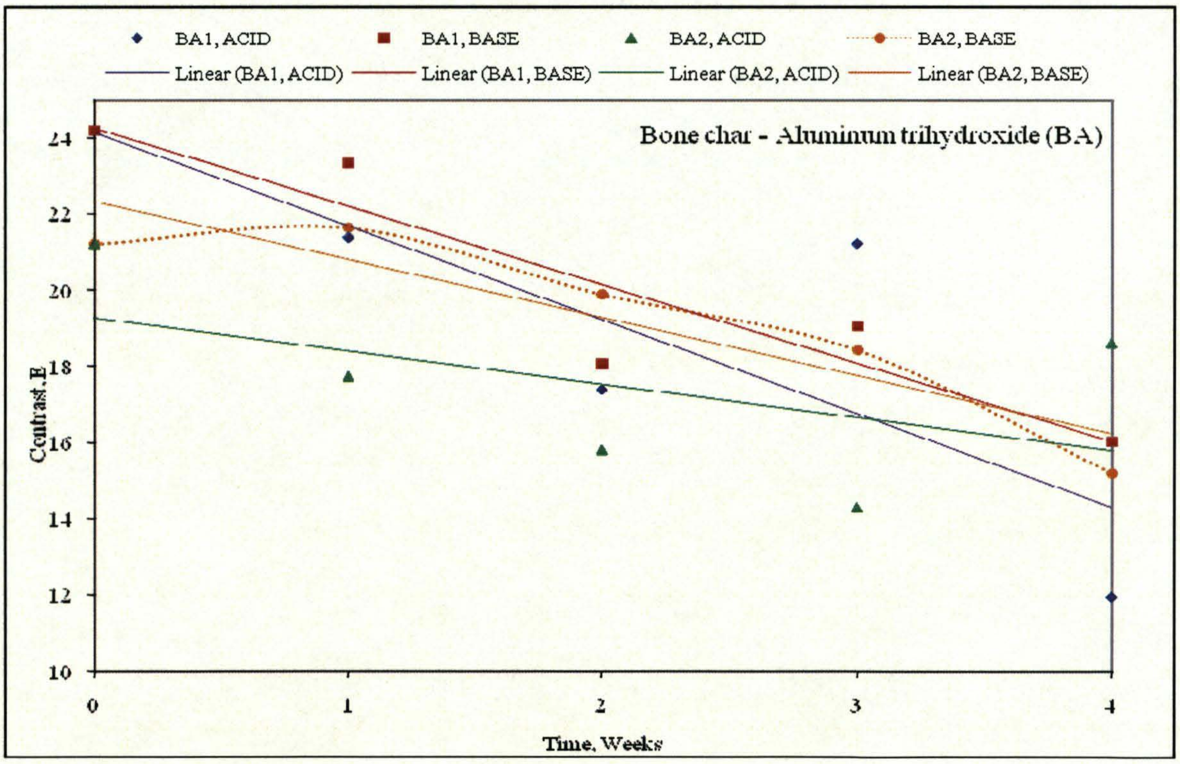

Figure 8.3.4 Durability Analysis results for Bone char + Aluminium trihydroxide (BA).

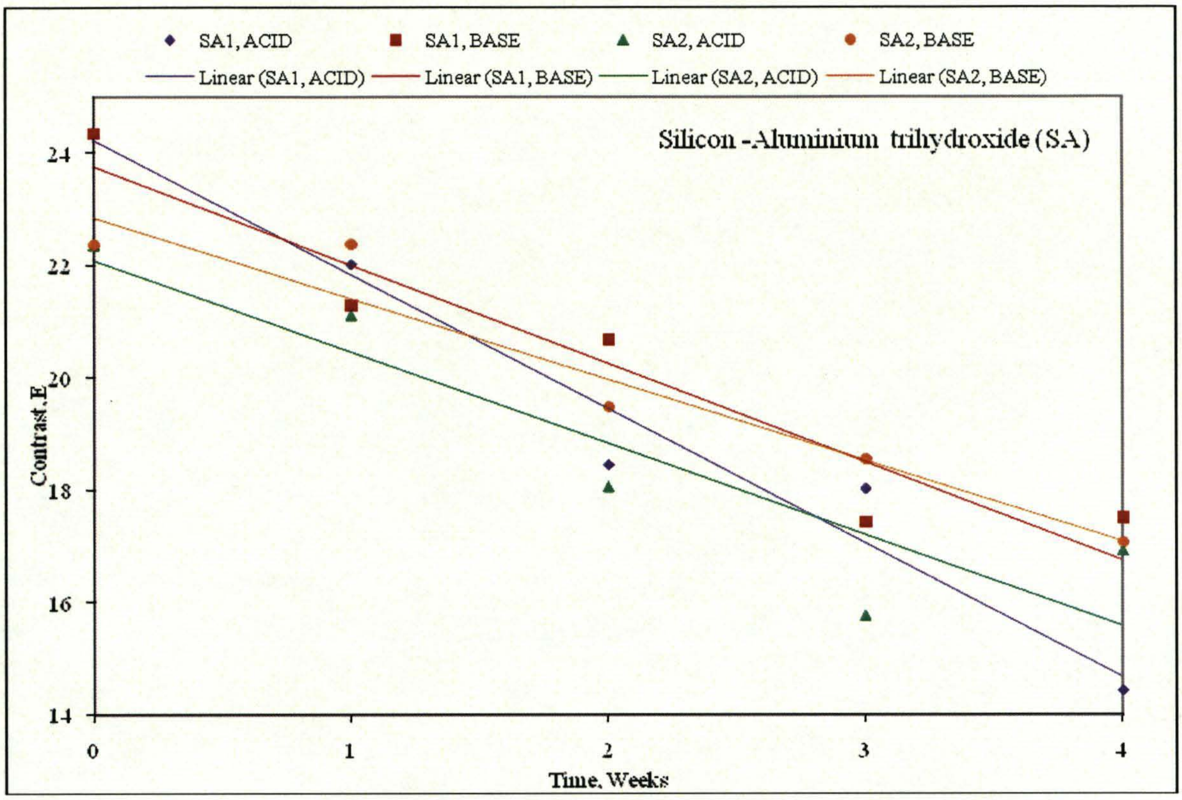

Figure 8.3.5 Durability Analysis results for Silicon + Aluminium trihydroxide (SA)