Calibration for Thermal Paint Chemistry

Harriet E. Cameron

University of New South Wales at the Australian Defence Force Academy

A greater understanding of hypersonic flow will result in a wider use of hypersonic vehicles for both military and civilian applications. There are still many uncertainties that exist within a hypersonic flow, in particular, the prediction of temperatures on the surface of hypersonic vehicles. One method to measure the high temperatures is the use of permanent change thermal paints. The understanding of thermal paints is slowly increasing, although there are still a lot of unknowns that exist. The aim of this report is to explore the relationship between the colour and the chemical behaviour of thermal paints while under steady state heating. Using steady state heating, the chemical properties of thermal paints can be analysed at set intervals of the colour change process. This report looks at establishing the framework for correlating the temperature-dependent behaviour of permanent change thermal paints to their chemical behaviour, based on an analysis of results interpreted from spectral analysis. It is anticipated that this data will facilitate the understanding of permanent change thermal paints for the measurement of the temperature distribution of recovered hypersonic vehicles.

Contents

Nomenclature ......................................................................................................................... 2

I. Introduction .......................................................................................................................... 2

II. Scope ................................................................................................................................. 3

III. Hypersonic Flight ............................................................................................................. 3

A. Aerodynamic Heating ........................................................................................................ 3

B. Methods for Measuring Temperature during Hypersonic Heating .............................. 4

IV. Applications of Permanent Change Thermal Paints ...................................................... 5

V. Chemistry of Thermal Paints ............................................................................................ 6

A. Transition Metals and Complex Ions ................................................................................ 7

1. The Chemical Background and Electron Energy States ............................................... 7

2. Crystal Field Theory ......................................................................................................... 8

VI. Methods for Measuring the Colour and Chemistry ......................................................... 9

A. Colour Measurement Methods ......................................................................................... 9

1. RGB/HSV Scale Measurement ....................................................................................... 9

2. Reflectance/ Absorbance Spectrometry ..................................................................... 10

B. X-Ray Fluorescence and Fourier Transform Infrared Spectrometry .......................... 11

VII. Previous Calibration Techniques of Thermal Paints .................................................... 12

VIII. Project Methodology ..................................................................................................... 13

A. X-Ray Fluorescence Spectrometry ............................................................................. 13

B. Equipment Preparation .................................................................................................. 13
APPENDICES (In supplementary document)

Appendix A. X-Ray Fluorescence Spectrometer Results  A1
Appendix B. Reflectance and Absorbance Spectrometer Results  A2
Appendix C. Full FTIR Spectrometer Results  A3

Nomenclature

Terms:
\( KBr \) = Potassium Bromide
\( FTIR \) = Fourier Transform Infrared
\( PMA \) = Poly Methyl Acrylate
\( XRF \) = X-Ray Fluorescence

Variables:
\( T \) = Temperature [°K]
\( c \) = Volumetric heat capacity [J/m3]
\( t \) = Time [s]
\( k \) = Thermal conductivity coefficient
\( \sigma \) = Stefan – Boltzmann
\( A \) = Surface Area of the sample
\( e \) = Emissivity
\( dT \) = Change in Temperature
\( q \) = Heat Transfer.

1. Introduction

Vehicles at hypersonic speeds experience extreme surface temperatures that can ultimately lead to their failure. The failure is typically a result of the surface temperatures affecting the vehicle in two ways; degradation of the mechanical properties of the material such that it cannot support the flight loads; and expansion of the vehicle structure causing thermal stresses beyond the capabilities of the material (Neely & Tjong, 2008). Permanent change thermal paints are used to predict the surface temperature experienced by hypersonic vehicles since the initial colour of the paint changes as the surface is heated. The final colour that the paint reaches is dependent upon the temperature that the surface is exposed to and for what period of time.

Current practice is to analyse the final colour using colour charts that are supplied by the manufacturer of the paint. Kruger (2009) and Neely and Tjong (2008) have shown that the resulting colour may indicate two possible exposed temperatures as the colour can be achieved by either a high temperature for a short period or a
lower temperature for a longer period of time. Further understanding could be gained by exploring the relationship between the colour and chemical behaviour of the thermal paints.

When vehicles experience hypersonic speeds, the total time that the vehicle is in hypersonic flow is generally a very small time. This time can sometimes be too small for a colour change in thermal paints to occur. The aim of this thesis is to explore the relationship between the colour and chemical behaviour of thermal paints while under steady-state heating. It is desired that a relationship between colour and chemistry with a time dependency (under transient heating) will eventually be explored, although to do this, the steady-state must first be explored to find the fundamentals of the chemical composition that changes during heating.

II. Scope

The project aims to explore the relationship between the colour and chemistry of thermal paints. This was to be done experimentally and while under steady-state heating. Upon recommendations from previous work in undergraduate studies, this project aims to explore the mechanisms governing the paint colour, the fundamental chemical reactions that the paints experience during heating and examine if the colour and chemistry of the paint can be related.

It is outlined further in this report that the change in colour of a thermal paint is time dependent and rapid temperature increases in short time frames is not sufficient to change the colour, but may activate the chemical reaction that causes the colour change. Thus the steady state measurements will be useful for transient responses in the future with further analysis. Therefore this project aims to set up the experimental procedure for analysis of a chemical-colour relationship as a full chemical analysis requires that the steady state response be known before applying the method for a transient response.

In order to explore the steady state response, firstly the elements within all the available paint types were analysed using an X-Ray Fluorescence (XRF) Spectrometry. As there are two different materials used in this experiment, their properties had to be analysed so that the time for both materials to reach a steady state temperature when placed into the oven could be found. This resulted in conducting a computer analysis to determine the soak times for the test materials. Lastly, the change in the colour of the thermal paint will be analysed using reflectance spectrometry and the chemical species were explored using a Fourier Transformation Infrared Spectrophotometer (FTIR). All of these processes will be explained in detail after the relevant literature review has been presented.

III. Hypersonic Flight

The speed of sound is classified as Mach 1 and hypersonic speeds, as a rule of thumb, are speeds at or greater than Mach 5 (Sears, 1954). Hypersonic flight was first achieved by a modified V-2 Rocket on February 24, 1949 reaching Mach 7.6 (Hallion, 2005) yet burned up upon re-entry into the atmosphere. The first manned hypersonic flight took place on 12 April 1961 with Yuri A. Gagarin, age 27, piloting Vostok 1.

As the flow passes through a shock wave, there is an abrupt increase in several of its properties; temperature, pressure and density. Further to this, at high Mach numbers, the flow field becomes dominated by four physical phenomena. At around Mach 5, these phenomena become distinct enough that they cannot be discounted at hypersonic speeds and are referred to as a separate theory of flow. The four phenomena are an increase in entropy, boundary layer thickness and aerodynamic heating and a decrease in shock layer (Anderson, 2003). The most significant to vehicle design is the aerodynamic heating as this can cause structural failure.

A. Aerodynamic Heating

There is a large amount of kinetic energy contained within a hypersonic flow. This kinetic energy is transferred to thermal energy when the flow undergoes sudden deceleration at the vehicles leading edges creating a shock. At high Mach numbers, ionisation and dissociation of the gases occurs within the flow behind the shock. The kinetic energy also becomes dissipated by friction in the boundary layer, causing a very high temperature rise within the boundary layer. Also due to the sudden deceleration, the region between a blunt body and a shock wave at high speeds can also reach extreme temperatures (Anderson, 2003). Figure 1 demonstrates these extreme temperature conditions on the leading surface of a supersonic combustion ramjet (scramjet) over a short period of time.
The sudden high temperature rise creates a challenge when designing vehicles for hypersonic flight. The materials used on the vehicle must be strong enough to withstand the high thermal-loading, but still be light enough to achieve good performance results. The hot gases created affect the loads on the surface and the energy flux (Bertin & Cummings, 2006). These loads must be taken into account when designing hypersonic test vehicles otherwise failure can occur. The thermal loading that is applied by the temperature can degrade the strength and stiffness properties of the material and also deform the structure, leading to failure (Neely & Tjong, 2008).

There have been several methods employed to overcome the heating problem. The space capsules such as the Mercury or Apollo used thick heat shields that are designed to absorb the heat and break off, carrying the heat away. A more advanced and reusable method is the use of heat tiles that absorb large amounts of heat, up to 3400 °F, or 2145 °K (Madison, 2006). The material has a very low thermal conductivity, and so any surface heat energy that is applied is mostly reflected and given off as light. Each of the tiles are very expensive to apply and maintain. Other solutions to surface heating include circulating a cold liquid or the vehicles fuel through the leading edges and surfaces most susceptible to heating. The liquid acts as a heat sink, absorbs some of the thermal energy in the surface and carrying it away from the surface to other parts of the vehicle. This can also benefit the efficiency of combustion in the engine as it pre-heats the fuel; however the process is complicated and expensive.

Heating is a major problem for the surface of vehicles, but at shock-shock or shock-boundary layer interactions the peak temperatures can exceed 11000 degrees Kelvin (Anderson, 2006). Due to their uncertain nature, locations of where these interactions will occur are unpredictable. This highlights the importance of using correct materials and having an accurate method to gain a global measurement of the temperatures that the vehicles surface is exposed to in hypersonic flows.

B. Methods for Measuring Temperature during Hypersonic Heating

There are several methods for measuring the surface temperature that have been established and are currently in use; each with their own advantages and disadvantages. Thermocouples, laser based techniques (which are commonly used in hypersonic test facilities) and permanent change thermal paints are all employed methods of measuring the temperature in a hypersonic flow.

Common practise when measuring the surface temperature of a component is the use of surface mounted thermocouples or thermo-resistors. One method for applying thermocouples is described by Bird et al (1997): A small groove of 0.45mm deep and wide is machined at a point of interest into the surface of the test component. The thermocouple cable, approximately 0.3mm in diameter is then place into the groove, and the excess space filled with a nickel (Ni) based vacuum furnace braze if possible, or with a nickel aluminium (NiAl) alloy spray. The excess is then removed by grinding, to leave as little disruption to the flow as possible (Bird et al, 1997).
Thermocouples have been widely used in aeronautical applications, and produce quite accurate results. However, there are several disadvantages in the use of thermocouples or thermo-resistors. This is an intrusive method where the installation can become costly. The grooves that have to be machined into the surface can compromise the structural integrity prior to testing and can alter the heat transfer through the material (Bird et al, 1997).

The indicated temperature using thermocouples and laser based techniques display the real-time temperature, which means that as the flow slows and cools, the indicated temperature also changes. Extra equipment is required for a permanent record of the peak temperature when using these methods. Further to this, thermocouples and thermo-resistors can only give discrete point measurements of the temperature. For the design of any supersonic vehicle, it is desired to have a global temperature map of the entire surface (Tracy, 2006).

As it can be difficult to predict the locations of shock-boundary layer and shock-shock interactions, the useful data that can be collected from thermocouples for material design is limited. Permanent change thermal paints are a superior way to globally map the surface temperature distribution and overcome this short fall. The use of permanent colour change thermal paints does not require any additional recording equipment as once the paint is heated the colour remains changed. The application is considered to be non-intrusive and the paints do not affect the surface temperature (Neely & Tjong, 2008). A great benefit of permanent change thermal paints is that they can be applied to component’s surface of any complex geometry and provide a permanent record of the peak temperatures reached and a global map of the surface temperature.

One problem that can arise from the use of thermal paints is if the exposure time of the maximum temperature is very small. In this case, the chemical reaction would not have had enough time to complete the colour transition for the applied temperature and the paints may not give a true reading of the maximum temperature. Permanent change thermal paints are temperature-time dependent which can make the analysis of the final colour difficult. Nonetheless, even with this short coming, using permanent change thermal paint is the optimum way to map a components surface temperature distribution.

IV. Applications of Permanent Change Thermal Paints

Prior to World War II, materials with an ability to change colour on reaching certain temperatures were discovered. These materials were developed so that they could be easily applied when testing equipment that experience high temperatures when in use. As the paint change colour after a thermal energy input, they were named permanent change thermal paints. Using this method of testing provides an easy estimate of a components peak temperature.

It was not until after WWII that an international study of these materials and their compounds was released. The study showed that these materials contained of temperature sensitive pigments that would change colour when given a certain amount of thermal energy. The pigments consisted of transition metals and it was also found that elements such as cobalt, manganese and copper produced the best results, as tests could be reproduced to give the same results (Cowling et al, 1953).

Thermal paints can be employed as either single-change or multiple-change colour transition paints. As the name suggests, single-change thermal paints undergo only one transition of colour, where multi change can transit through several different colours. The main attraction of using thermal paints to model the distribution of temperature over a surface is the ability to obtain a global temperature profile of the component under examination, where thermocouples and other such methods can only give point temperatures (Bird et al, 1997).

Temperature analysis using thermal paints has been achieved in several types of research. Thermal paints were first used to analyse the temperatures of airfoils and surfaces of components. Thermal paints were used to determine the aerodynamic heating rate of a surface undergoing heating at the NASA Langley Research Centre in 1959. Due to the complexities of thermal paints, a program was put in place at the Research Centre for the continuation of research for perfecting the use of thermal paints. One of the initial methods to map the relation between temperature and colour was to use a motion picture camera to find the rate of the heat transferred through the colour change over a time period, where the colour change indicated the changing temperature (Jones & Hunt, 1964).

Once thermal paints were shown to produce good quality results, they were employed on rotating elements of equipment. Permanent change thermal paints have been employed in the aeronautical industry by Rolls Royce since the 1950’s. Rolls-Royce commercial aero engine company successfully analysed temperatures using thermal paints on the rotating turbine blades of gas turbine engines (Bird et al, 1997). Rolls-Royce found that using single-change colour paints could become difficult when analysing a large temperature variance area, as they only give one indication.

Their next approach was to use a combination of paints, e.g. five different paints applied to five blades, which would achieve a temperature profile. Figure 2 shows an example of how thermal paints are applied to gas
turbine blades from a blue to yellow colour, left to right. This gave only a good indication of the temperature reached by the blades. As this proved problematic with some testing arrangements, Rolls-Royce commenced the development of a range of multi-change paints in the mid 1960’s (Bird et al, 1997).

The successful application of thermal paints in the harsh environment of the gas turbine engine showed that thermal paints would be suitable for applications in hypersonic flight testing. It is now common practise to use permanent change thermal paints in the aerospace industry, and engineering in general. As long as the coatings of the paint are kept thin, the application of the paint is considered as nonintrusive. Permanent change thermal paint application provides a full surface temperature profile but it can be time consuming to determine the peak temperature from the resultant colour.

\[V. \quad \text{Chemistry of Thermal Paints}\]

Research from the 1950’s concluded that suitable paints for thermal applications must consist of a resin (or binder solution) and a transition metal pigment which is contained within the resin. The resin must be sufficiently stable enough to withstand elevated temperatures without changing structure. Within the total composition of the resin and pigments, it is the pigments that change colour at different temperatures and so to give accurate readings, the resin must not change colour. Cowling et al. evaluated that a “solution of methacrylates resin, properly plasticized, provides an adequate vehicle for carrying pigments.” Resins used in industrial applications are acrylic based and a commonly used solution is poly methylacrylate (PMA). PMA resin is able to be heated to high temperatures, and remain stable (Neely & Tracy, 2006).

Pigments used in thermal paints permanently change colour, as a result, real-time monitoring is not required for analysis. An object can appear red if it absorbs all light, but reflects the red component. The same object can also appear red if it reflects all colours except green, the complimentary colour of red. Figure 3 shows a basic colour wheel of the colours and approximate wavelengths.

When the colour change occurs, this indicates that a physical change in the chemistry has also occurred such that light is reflected at a different wavelength which appears as a different colour. The physical changes within the paint can be understood with a basic knowledge of the electron configuration of transition metals, which are commonly used for pigments and other complex ions. Crystal field theory describes the nature of the bonding in transition metal complexes.
A. Transition Metals and Complex Ions

The driving force of the colour change in the thermal paint is the ability of the transition metals to change energy states and to form complex ions. Transition metals have a quality that is responsible for resulting in a distinct colour. This is that the change in an energy state and when a complex ion is formed, the bonds within the compounds are changed. The understanding of transition metals and knowledge of basic chemical principles is necessary to establish a base for this thesis as such this body of knowledge is described further in the following section.

1. The Chemical Background and Electron Energy States

All elements consist of a nucleus that is surrounded by electrons. When the electrons are at different states of energy within the same shell, they are called an “orbital”. In quantum mechanics, four quantum numbers are required to describe the distribution of electrons. These are the principal (\(n\)), angular momentum (\(l\)), magnetic (\(m\)) and electron spin (\(m_s\)) quantum numbers. To understand the behaviour of transition metals for the use of thermal paints, the principal, angular momentum and magnetic quantum numbers must be identified. The principal quantum number, \(n\), can have integral values 1, 2, 3 and so on, which relates to the energy of an orbital. The principal quantum number, \(n\), also relates to the average distance from the nucleus to the electron for a particular orbital: the greater the value of \(n\), the greater the distance from the nucleus to the electron and so the greater the radius of the orbital.

The shape of the orbital is determined by the angular momentum quantum number (\(l\)) and is related to the principal quantum number, \(n\). For each orbital, the range of \(l\) values is from 0 to \(n-1\) values of \(l\) in an orbital, where the different values of \(l\) are designated by letters \(s, p, d, f, g, h\) and so on through the alphabet from \(h\). For example if \(n = 2\), then \(n-1 = 1\), and there are two values of \(l\), 0 and 1, represented by \(s\) and \(p\). This is shown in table 1.

<table>
<thead>
<tr>
<th>(l)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name of orbital</td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>f</td>
<td>g</td>
<td>h</td>
</tr>
</tbody>
</table>

Table 1. Name of orbital for values of \(l\) (Based on Chang, 2007)

An orbital at the same \(n\) value are collectively called a shell. When one or more orbital has the same \(n\) and \(l\) values, these are referred to as a subshell. For example, when the shell is comprised of \(n = 3\), there are three values of \(l\), being \(s, p\) and \(d\). These subshells are denoted as \(3s, 3p\) and \(3d\).
Now that the energy state and shape of the electrons can be determined, the orientation of the orbital is also important. The magnetic quantum number, $m_l$, describes the orientation of the orbital. The magnetic quantum number relies on the angular momentum to determine the number of orientations of the subshells. For a value of $l$, there are $(2l + 1)$ integral values of $m_l$. The values of $m_l$ range from $-l$, $(-l + 1)$ $\ldots$ $0$ $\ldots$ $(+l - 1)$, $+l$. For example, when $n = 3$, $l$ ranges from 0 to $n-1$, and so three values of $l$. For $l = 2$ (i.e. the $d$ orbitals), there are $2l + 1$ values of $m_l$, namely $-2$, $-1$, 0, 1, and 2. These five values of $m_l$ indicate that there are five orbitals in the subshell with a particular $l$ value (Chang 2007).

Complex ions are defined as ‘an ion containing a central metal cation (an ion with fewer electrons than protons) bonded to one or more molecules or ions’ (Chang, 2007). A Lewis acid or Lewis base are terms for describing how molecules interact with ions and one another. A substance that can accept a pair of electrons is called a Lewis acid, and one that can donate a pair of electrons is called a Lewis base. Lewis acids and bases are important for coordination compounds and crystal field theory. For example, cobalt (II) chloride is pink due to the presence of Co(H$_2$O)$_6^{2+}$ ions, once HCl is added, it turns blue as a result of the formation of CoCl$_4^{2-}$ i.e. [Co$^{2+}$(aq) + 4Cl$^-$ (aq) $\leftrightarrow$ CoCl$_4^{2-}$(aq)] as shown in figure 4. This is a simple demonstration of how a transition metal changes colour when starting with a complex ion and adding a solution. This colour change can also happen if there is a change in energy states brought on by a change in temperature. This is described in crystal field theory (Chang, 2007).

2. Crystal Field Theory

Crystal field theory describes the nature of the bonding in transition metals and complex ions in terms of electrostatic forces. These forces are the attraction between the positive metal ion and the negatively charged ligand, or an interaction between the electrostatic repulsion between the lone pairs on the ligands and the electrons in the $d$ orbitals of the metals. Ligands are the molecules or ions that surround the metal in a complex ion. The interaction between a metal ion and the ligand can be thought of as a Lewis acid-base reaction. Every ligand has at least one unshared pair of valence electrons, such as H$_2$O, NH$_3$, or Cl. Ligands act as the Lewis bases and a transition metal atom acts as the Lewis acid. An example of how complex ions have been used for medical aid, figure 5 (a) shows the ligand ethylenediaminetetraacetate (EDTA), a polydentate (many atoms are present) ligand, used in the treatment of lead poisoning. In this example, the donor atoms are the four Oxygen and two Nitrogen atoms. The six donor atoms form a very stable complex ion with lead, figure 5 (b). When EDTA has entered the body, it forms the complex ion with lead and is safely removed from the blood and tissue and excreted from the body (Chang, 2007).

![Figure 4. Co(H$_2$O)$_6^{2+}$ ions with HCl solution added and the colour change. (Based on Chang, 2007)](image)

![Figure 5. (a) EDTA ligand and (b) EDTA complex of lead (Chang, 2006).](image)
Figure 6 shows, each d orbital can have a different orientation but all have the same energy. However, the orientation of the orbital can create a relative difference in energy. Two of the five 3d orbitals, d_{xy}, d_{yz} and d_{xz} have a relatively increased amount of energy as compared to the d_{x^2-y^2} and d_{z^2} orbitals. Crystal field splitting is the difference in energy between two sets of d orbitals in a metal ligand when ligands are present (Chang, 2007). The magnitude has a direct effect on the colour properties of complex ions and depends on the metal and nature of the ligands.

Transition metals usually have an incompletely filled d subshell, or easily give rise to ions with incomplete d subshells. This quality is accountable for several properties, including a distinct colour and a great a tendency to form complex ions. Transition metals have more than one oxidation state, which means they have the ability to form complex ions and allows them to act as a Lewis acid or a Lewis base. Crystal field theory is relevant to thermal paints as the pigments are transition metals and undergo crystal field splitting when excited with energy, such as an input of heat. The best way to measure crystal field splitting is to use Fourier Transformation Infrared Spectrometry to determine the wavelength at which the light is absorbed. As the energy increases there is a change in the bonds between the metals and ligands that changes the energy of the orbital. This means that a different wavelength is emitted and different colour is observed.

VI. Methods for Measuring the Colour and Chemistry

To explore the relationship between the colour and chemical behaviour of thermal paints, a method must be established to quantify both variables. There are several ways to measure colour, including using cameras that determine the amount of red, green and blue that combined, give the final colour. Reflectance spectrometry is another method that results in a spectrum of the reflected wavelengths of light and the percentage the source light that is reflected.

To measure the chemical species present in the samples, Fourier Transform Infrared Spectrometry is used. It is a requirement for FTIR spectrometry to use potassium bromide (KBr) discs as the testing material so that the infrared laser can penetrate through the material and an absorption spectrum is detected. Using FTIR spectrometry, it can be determined the change in the absorbance of certain wavelengths, where each wavelength indicates a different chemical compound. All measurement methods are described below.

A. Colour Measurement Methods

1. RGB/HSV Scale Measurement

The measurement of colour can be done in several ways. Previous studies of a similar nature have quantified the colour change by using a Red Green Blue (RGB) scale. This is a very simple way to measure colour, and is based on how the human eye responds to colour. That is a human eye contains a number of cones, each of which is sensitive to the primary colours red, blue and green. The combination of the three colours over a number of cone responses allows the human eye to detect colour. Except under extreme darkness, all objects reflect some
measure of light from the visible spectrum. This light can be quantified and given a value as to the amount of red, blue and green that it consists of. An RGB scale denotes the amount of red, green and blue that is reflected from a sample giving the final colour with three values. With the use of computers and apparatus, we can identify the amount of red, green and blue which makes up the perceived colour (Griffin, 1996).

The perception of colour is sensitive to not only the individual, but also to the magnitude, quantity and wavelength of light from a source illuminating a sample as lighting and the purity of colour have a strong influence on the perceived colour. The RGB scale was developed to give a colour measurement system that describes a colour based on the combination of the three values.

Another method to quantify colour is to use the hue-saturation-value (HSV) co-ordinate system. The HSV system is a geometrical representation where every colour is assigned a value based on the wavelength, intensity and lightness. Both the RGB and HSV scales are more accurate at defining a colour than how a human could interpret it. Using the RGB of HSV scale is an accurate way to define colour, which in turn can result in a higher accuracy for determining the resultant peak temperature thermal paints undergo.

It can be shown using the computer software “MS Paint” how the RGB and HSV (aka HSL in Paint) scale changes with the colour, as in figure 7. As described by these different co-ordinate systems, colour must be represented by at least three variables and this greatly complicates colour data analysis. Defining a colour change depends on the measurement technique used. For this study, it was determined that using an RGB/HSV scale would be overly complicated and not add to the overall findings for quantifying the colour change.

![Figure 7. Red, green, blue and “brown” as a display of colour measurement using MS Paint with a RGB and HSV scale.](image)

2. Reflectance/Absorbance Spectrometry

Another method for quantifying colour is the use of spectroscopy. A spectrometer is an instrument that detects the characteristics of light scattered, emitted or absorbed by atoms and molecules in the ultraviolet and visible wavelength spectrum. Transitions between energy levels are stimulated by or emit ultraviolet, visible or near infrared radiation. When the spectrometer irradiates the sample, both the absorption and reflectance at a given frequency are stimulated. The reflectance of energy in the form of photons at different wavelengths and can be recorded by a spectrometer as the detector scans a set range of wavelengths. A transformation can then be done by the computer program connected to the spectrometer to determine the absorbance of the sample from the reflectance.

When the nucleus of a molecule experiences no net force from the electrons and other nuclei in the molecule, they are in the ‘ground state.’ When the molecules undergo a transition of energy, such as an increase in temperature, they are subjected to a change in force. When a molecule undergoes a change of energy state from a high energy state to a lower one, it emits the excess energy as a photon, and for an increase in energy state, there is absorption of energy. The photons emitted or absorbed at an energy level of several electronvolts (where 1 eV, is equivalent to 100 kJmol⁻¹) are in the visible or ultraviolet spectrum. For a change of colour to occur in the samples with thermal paint applied, the combination of molecules within the paint pigments must be altered. Several electronvolts of energy is needed to change the distribution of molecules and the bonds between the metals and ligands (Chang, 2007). With the bonds are altered, the energy of the orbital changes shown in figure 5 and 6, resulting in a different peak wavelength and the percentage of the original light being reflected will also change, resulting in a colour change. This amount of energy can come from in a rise in temperature.

Energy levels can be explored by examining the frequencies present in the radiation scattered by molecules. For the purpose of this report, emissions and absorptions of the visible light spectrum (approximately 400 – 700nm) will be concentrated on. For a liquid or solid, the absorption or reflection of wavelengths results in a
range of peaks or troughs across the visible spectrum. Figure 8 demonstrates how spectrometry can determine the reflected wavelengths for a sample of the SC 155 without any heat having been applied.

Figure 8. Reflected spectra for SC 155 sample (right) without any heat applied.

Note that it reflects in the green (~500nm) region. This sample of thermal paint SC155 is described as a shade of green, as it has absorbed all other components of visible light except the green component. For this study, the use of spectroscopy was chosen as the method for measuring the colour change as the results produce a lot of information that can be easily interpreted, or represented in alternate forms giving indications (for example) of the peak amplitude of the spectra and at what wavelength the peak occurs, for all temperatures. This is shown in the results, section IX, C.

B. X-Ray Fluorescence and Fourier Transform Infrared Spectrometry

To examine the chemistry of the thermal paints, two items of laboratory equipment are used; X-Ray Fluorescence (XRF) Spectrometer and Fourier Transform Infrared (FTIR) Spectrometer. XRF spectrometry is a physical technique for elemental analysis. Elements emit characteristic radiation when subjected to the appropriate excitation. The emission of such radiation produces characteristic line spectra and can be induced by the impact of accelerated x-ray photons. Once the atom emits radiation in the form of an electron, the atom becomes ionised (Tertian & Claissé, 1982). The specifics have been discussed in section IV and V, a, 2. The XRF spectrometer consists of an exciter that emits x-ray photons onto the sample and a detector picks up the radiation emitted by the ionised atom. The set up is shown in figure 9. The XRF spectrometer produces results that give the elements contained within the sample and to what percentage (by mass) they are present. An example result of the MC 165-2 paint is shown in figure 10.

Figure 9. Internals of the X-Ray Fluorescence Spectrometer (Shimadzu, 2010).
The second method for analysing the chemistry is to use a Fourier Transform Infrared (FTIR) spectrometer. The FTIR spectrometer radiates the sample and uses a detector to record the wavelengths that are absorbed by the samples. Molecules absorb at specific frequencies which are characteristic to the structure of the molecule. Knowing this, using an FTIR spectrometer, it can be determined from the frequency of the absorbed radiation what species of chemical bonds are present in the sample being irradiated. As each group of chemical species has different vibration energy. In this case, the sample is irradiated by an infrared laser. Thus the frequency of the bonded group is associated with a particular bond type. The FTIR spectrometer results in a spectrum of peaks and troughs of the absorbed radiation from the sample. The samples were all tested at 4000 – 400 cm⁻¹ to gain a large range of possible species to analyse. An example result is shown in figure 11 for MC 165-2 paint prior to any heating.

Figure 11. The FTIR results for MC 165-2 before heating.

The nature of thermal paints has been discussed in section V of this paper. It has been found from this study that common elements within the paint are silicon and chlorine. Remembering that ligands act as a Lewis base and a transition metal atoms act as a Lewis acid, it has been found that Cl and Si are present in the majority of the 15 types of paint tested under XRF spectrometry and determined that Cl and Si (separately or together) acts as the resin in the majority of thermal paints. These results were found using a Shimadzu EDX-800HS Energy Dispersive X-Ray Fluorescence Spectrometer and can be found in the results section IX.

VII. Previous Calibration Techniques of Thermal Paints

Techniques that have been used for the calibration of thermal paints involve the heating of a sample of to a known temperature for a range of time periods and the colour of the sample is then identified using several different methods. Neely and Tjong (2008) conducted experiments to relate the time-temperature-colour dependencies of thermal paints. The experiments resulted in the production of easy to use visual colour charts. Several single and multi colour change paints were exposed to known temperatures for different soak periods and the colour analysed, as shown in figure 12. Neely and Tjong (2008) determined that it was needed to further examine the fundamental chemical reactions that thermal paints experience during heating.

Kruger (2009) looked at the transient response of thermal paints using an oxy-acetylene torch to apply heat to the samples for a range of time periods and a range of temperatures. Kruger also analysed the colour using several different methods to measure the colour. This process simulates hypersonic heating where times ranged from 0 – 60 seconds, and temperatures experienced were over 1000°C. Kruger determined that further analysis to determine the most suitable method of quantifying the colour change of thermal paints with a minimum number of parameters was required. Kruger also determined that additional work was to be undertaken in terms
of colour and chemical analysis, to firstly understand the correlation between spectral and digital measurement techniques in the visible spectrum, and secondly to determine the change in chemical composition of the thermal paints using the X-Ray and IR regions of the spectrum. The results of Kruger’s study showed that these methods produce useful and simple data of the colour-temperature relationship as a function of time, but is only accurate provided the same lighting conditions are met for the RGB colour analysis (Kruger, 2009).

This report looks at the chemical reaction that occurs as the paints are heated in a steady-state condition. It is hypothesised from previous analysis that the amount of the colour change the paint has undergone will be proportional to the amount of the chemical reaction that has been completed. This study establishes the experimental procedure for a steady-state heating analysis, looking at correlating the colour to the chemistry and can be adjusted for future work while under transient heating.

Figure 12. Colour map for a selection of single-change and multi-change thermal paints (Neely and Tracy, 2006)

VIII. Project Methodology

As stated previously in section II, this project was conducted in four distinct parts; firstly the elements within all the available paint types were analysed using an X-Ray Fluorescence (XRF) Spectrometry, then a computer analysis was performed to determine the soak times for the test materials. Lastly, the change in the colour of the thermal paint was analysed using reflectance spectrometry and the chemical species were explored using a Fourier Transformation Infrared Spectrophotometer (FTIR). All of these processes will now be explained in turn as well as a description of the preparation process for the equipment.

A. X-Ray Fluorescence Spectrometry

The first part of conducting the experiment for this study was to select which paints were to be used. A total of three paints, two SC and one MC, were to be selected for the study. The selection of the three paints was based upon the results of analysing all 15 paints under the XRF spectrometer. The paints which contained one transition metal as the dominant element in the paint would be most suitable for testing. As described above in section V, A, the transition metal reaction within the paint compound causes the change in colour, and so selecting a thermal paint with as few or even only one transitional metal would make data easier to analyse and thus the relationship between chemical elements within the paint and the colour could be more accurately explored. The results of this process are detailed below in the results section.

B. Equipment Preparation

Within the sample test pack of permanent change thermal paints used in this project there are fifteen paints, each have a different initial colour and change colour at different temperatures. Permanent-change thermal paints can be separated into two groups: Single Change (SC) and Multiple Change (MC). Within this sample pack, there are 8 SC and 7 MC paints. For explanatory purposes the name of paint has two parts to it, the first either SC or MC, indicates whether the paint has a single or multiple change of colour, and the second comprising of three digits, indicates the temperature at which the paint undergoes the first colour change when heated at that temperature for ten minutes. However this is only true for SC paints, in the case of MC paints, after the first three digits, there is a dash and another number, e.g. MC 570-12. This indicates the paint will have
multiple changes, where the first occurs at 570 degrees Celsius when heated for 10 minutes (as stated by the manufacture, TMC) and there are a total of twelve colour changes.

This design of this experiment was to heat the paint to a range of temperatures and at each temperature, identify the colour in wavelength, and the chemical species that are present. The relationship between the colour and the chemical species will then be attempted to be identified for a colour-chemistry relationship.

As there were two measuring techniques (colour and chemistry) for this study, it was required to have two types of materials to sample. These were metal plates and potassium bromide discs. Mild steel was chosen as the metal for the plates and the dimensions are 50x30x1.2 mm. The KBr discs were the required material to use the FTIR machine. Each KBr disc is 25mm in diameter and 4mm in thickness with a circular cross section. The mild steel plates had to be sand blasted on the side that was to be painted, as the initial galvanised surface was too smooth for the paint to adhere to well. Prior to painting the KBr discs, they were to be polished with PMA solvent to remove any previous paint or dirt. Any excess PMA from cleaning would not affect the paint applied as PMA was contained within each of the paints.

The metal plates were cut from a large sheet of mild steel, which was cheap, readily available and so there could be an unlimited number of plates made. The KBr discs were purchased from Strana, and were expensive, which meant due to availability of funds, a total of 12 discs were made available for this study. With the limited number of KBr discs, the first test paint was applied to 11 metal plates and 11 out of 12 KBr discs. The KBr discs can then be tested for the first paint and then all the KBr discs are needed to be cleaned before the next paint can be applied and tested. One of the KBr discs is kept clean for the background scan for the FTIR measurement. This reduces the amount of background noise and gives a clearer reading for the painted KBr discs being tested. To minimise uncertainty between the KBr discs and metal plates undergoing the same paint and temperature conditions, both would be placed into and removed from the oven at the same time.

For each of the selected paints, the temperatures that would be used were selected depending on the first colour change of the paint and the temperature range of the oven that was available. The temperatures that were selected for testing the three paints are shown in table 2.

![Figure 13. Pictures of SC155 Metal plates and KBr disc before heating, and SC155, SC367 MC165-2 after heating.](image-url)
Table 2. Selected Testing Temperatures for the Three Paint Types.

<table>
<thead>
<tr>
<th>Paint</th>
<th>Test Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC155</td>
<td>125 130 135 140 145 150 155 160 165 170</td>
</tr>
<tr>
<td>SC367</td>
<td>337 342 347 352 357 362 367 372 377 382</td>
</tr>
<tr>
<td>MC165-2</td>
<td>145 155 165 175 180 270 280 290 300 310</td>
</tr>
</tbody>
</table>

The third paint that was selected MC165-2, had two changes of colour. The first change would occur at 165 degrees Celsius after a ten minute heating. The second change, as specified by the manufacturer TMC, occurred at 280 degrees Celsius when heated for ten minutes and at 310 degrees Celsius when heated for 60 minutes. These colour changes are presented in figure 13, which shows the metal plates and KBr discs painted with SC155 before heating and all three paints after heating to the said temperatures. As the heating was determined to last 30 minutes to reach steady state heating by the computational analysis, it was presumed the second change for MC165-2 would occur at approximately 290 degrees Celsius. MC367 was tested at 145, 155, 165, 175, 180, 270, 280, 290, 300 and 310 degrees Celsius.

C. Computational Analysis Using Ansys

To determine a sufficient time for both material types (mild steel plate and KBr disc) to reach a steady-state temperature when heated in the oven, a computational analysis was done using Ansys. The manufacturer states that the paint will reach a colour change at a temperature after 10 minutes, although this does not take into account the materials used. As such the computational analysis conducted using Ansys determines the appropriate soak time for each of the samples, ensuring that for their specific properties, the material will have sufficient time to reach a steady state temperature.

Ansys is a computer program that was used to calculate the transient heating for both the mild steel plate and the KBr disc. Heat transfer from the oven to the material samples is done in three ways; convection, radiation and conduction. It was assumed that conduction would be too small to have an effect on the heating of the samples. Inputs for the specific heat capacity, density and thermal conductivity were required so the program could compute the heat transfer to the metal plate and KBr disc through convection and radiation from the oven.

The conductivity is different for each of the materials as the thermal conductivity constant, \( k \), is different for each material. The thermal conductivity for the KBr disk was 4.8 W/m\( \cdot \)K. The mild steel plates were taken as an average value for galvanised mild steel at 10 W/m\( \cdot \)K. The emissivity for each paint type was taken from previous studies to be 0.94, and on the surfaces of the KBr and mild steel plates that were not painted, their respective emissivities were 0.85 and 0.25. The specific heat capacity, emissivity and density information was found using MatWab (2010), a material property data site that is linked to the Ansys computer program.

The calculation of the heat transfer in Ansys is based on equations 1 and 2 where \( \sigma \) is the Stefan – Boltzmann 5.67 x 10\(^{-8}\) W/m\(^2\)K\(^4\).

\[
q = -k \ dT \\
q = A e \sigma \ dT^4
\]

Using Ansys was an easy way to roughly calculate the time for the materials to reach a steady-state temperature, and requires the user to input only several of the materials properties and no other computation is required by the user. A computational heat transfer analysis is recommended to be conducted should future experiments take place.

D. Reflectance and Absorbance Spectrometry

Precise measurement of the colour of the metal plates after heating was done by use of reflectance spectrometry. This type of spectrometry works by emitting light onto the surface of the testing sample and detectors scan a range of wavelengths to detect the reflected light and record their amplitude. Light is generated by a source lamp which is normally a tungsten lamp for the visible region of the spectrum. The sample will absorb a certain amount of the light at each wavelength and the remaining light is reflected and detected by a suitable detector in the spectrometer. The spectrometer is connected to a computer where a program from Shimadzu, interprets the results and displays them as a graph, measuring the reflectance of the sample as a percentage of the transmitted light. The reflectance spectrometers optics and electronics systems have a high sensitivity, and are able to make measurements at selected fixed wavelengths, or scan over a rage of wavelengths. For this experiment, the selected range to execute the scan was from 400 to 800nm; the visible
spectrum wavelength range plus some of the ultra violet (UV) and infrared (IR) spectrum. Once the scan for the reflectance was completed, the program performs a transformation to display the absorbance for each sample.

To ensure the surface of the metal does not interfere with the identification of the colour, the paint must be applied with a thick coating (at least 40μm thick) onto the metal plate. The results of the reflectance spectrometry does not directly give the colour of the sample, however it does give the spectra which can be used to imply colour. The results also produce a large amount of data that can be easily interpreted as a “colour change” and can also be represented in several different forms, including the peak amplitude of the spectra and at what wavelength the peak occurs, for all temperatures. This is discussed further in the results section.

It was also discussed as to whether taking spectrometer readings from a hand held spectrometer while heating would be a valuable addition to the collection of data. Initially, when the first notion was to heat the samples using a hot plate, this would be viable, although as the final decision was to heat the samples using an enclosed oven, this would not be possible. For future analysis based on this experiment, taking measurements using a hand held spectrometer would be a good way to collect data of the wavelength that is reflected as the sample is heated, giving a transient response. As this experiment is based upon steady-state analysis, this is not a necessity.

E. Fourier Transform Infrared Spectrometry

To examine the chemical compounds or species that are present within the paint sample, a thin coating of paint is applied to a potassium bromide (KBr) disc then placed into the Fourier Transformation Infrared Spectrometer (FTIR). Fourier transform infrared spectroscopy is an analytical technique that can be used for compositional analysis of coatings. The technique is based on the interaction of light with matter. Light, by nature, is electromagnetic radiation and has both wave-like and particle-like properties, which affects the interaction with matter. The molecules have energy levels that are electronic, vibration or rotational. Each electronic state has a low-energy, ground state and higher energy. The excited states are subdivided into vibration energy and rotational energy. The KBr sample is radiated with an infrared laser. This laser is detected once it has passed through the KBr disc. Knowing this, using an FTIR spectrometer, it can be determined from the frequency of the absorbed radiation what species of chemical elements or compounds are present in the sample, as each group of chemical species has different vibration energy. Thus the frequency of the bonded group is associated with a particular bond type. The absorbance of infrared radiation that excites molecules from the ground vibration state to a higher, excited vibration state provides information about molecular composition.

The FTIR Spectrometer allows the measurement of light energy intersection with molecule bonds to be recorded as absorbance or transmittance of infrared radiation by the sample material versus wavelength. The FTIR spectrometer results in a spectrum of peaks and troughs of the absorbed radiation from the sample. The samples were all tested at 4000 – 400 cm$^{-1}$ to gain a large range of possible species to analyse.

IX. Results

A. X-Ray Fluorescence Spectrometry

As stated above in the section on project methodology, the XRF spectrometer was used to determine the elemental composition of all 15 of the thermal paints. This is an important first step as the results of this test will enable the selection of three thermal paints, two SC and an MC for testing in the following procedures.

The results are displayed as a spectrum showing the dominant species contained within the sample. The results are also displayed as a percentage of each element present. Reasoning for conducting this experiment is to make sure that the chosen paints are the best possible options for the experiment. The ideal paint would contain a large percentage of one transition metal which could make it easier to analyse the FTIR results, which display the chemical species that are present in the paint. The results of this part of the experiment showed that the three paints that had a minimum of 40% of one transition metal present, which were SC 155, SC 367 and MC 165-2 with the dominant transition metal being copper, titanium and cobalt respectively. The results are shown in figure 14 a, b and c for the selected three paints SC155, SC367 and MC165-2 respectively. The results for all paints are available in Appendix A. As explained, the analysis of the results determined the three paints that would be suitable for using in this experiment. The paints that were preferable to use had a high concentration of one transition metal and were in line 4 of the periodic table (the first line of transition metals), with atomic numbers 22, 27 and 29 (Titanium, Cobalt and Copper respectively). There were several paints that were not suitable, MC 470-9, MC 490-10 and SC 550, as these paints contained lead, Pb, which could be dangerous to work with under basic safety conditions.
B. Computational Analysis Using Ansys

Ansys, a computational analysis program, was used to determine how the materials react when given a heat input from an oven. Ansys assisted with a basic heat transfer analysis to ensure that when the samples were to be removed from the oven, they would have reached a steady-state temperature. This type of analysis was conducted to compare how the two materials would react when placed in the oven and heated. As the metal plate has a higher thermal conductivity, the heat is easily transferred from the surrounding hot air to the metal plate and 10 minutes would be sufficient time for only the metal plates to remain in the oven. However, as the KBr discs have a much lower thermal conductivity, the surrounding hot air in the oven takes more time to raise the temperature of the KBr discs. The analysis for the KBr discs also showed that for the lower external temperatures, after 20 minutes the KBr discs are not yet at a steady state temperature. Therefore, based on the KBr disc transient heating results, the total time for both of the samples to be left in the oven was set at 30 minutes. The analysis also determined the maximum and minimum temperatures within the plate and disc. It is shown in the top half of figure 15 how the heat is distributed through the plate and disc. As the maximum difference between the maximum and minimum temperature was never more than 0.1°C, the internal distribution of heat would not be a factor for the samples that were to be tested.

The results for the computational analysis are shown below for the metal plates (left) and the KBr disc (right) at all temperatures. This analysis showed that a total time of 30 minutes in the oven was sufficient time to reach a steady-state. The overall goal of this experimental analysis was to avoid inaccurate collection of data, if the materials were left in the oven for too long or are taken out too soon.
C. Reflectance and Absorbance Spectrometry

It has previously been discussed how the reflectance spectrometer works and that it was desired to have a spectrum produced from the reflectance scan. However, the data from the reflectance spectrophotometer scans could only be saved as co-ordinates in a data file where the information could then be transferred to another computer and the data points could be inputted into MATLAB. Using MATLAB, the graphs could then be reproduced. The results for the reflectance and absorbance spectrometer for all three paints are in figure 16 and are contained in Appendix B.

Using the spectrum to imply colour is based on the wavelengths that are reflected or absorbed. Shown in figure 3 is a colour wheel, and it has been stated that if an objects surface reflects one component of visible light, say the red region (approximately 650 – 700 nm) or reflects all except that same region, the object will appear red. The reflected spectrum can also vary with regards to the amplitude of the peak wavelength. If the resultant reflected spectrum is a constant low percentage of the source light i.e. the majority of the source light is absorbed, the colour appears to be a very dark colour, as a true black body absorbs all light.

The results also produce a large amount of data that can be easily interpreted as a “colour change” and can also be represented in several different forms, including the peak amplitude of the spectra and at what wavelength the peak occurs, for all temperatures. This is discussed further in the results section.

The peak of the reflectance spectra of the SC 155 samples at each of the temperatures can be seen to move to the right, increasing in wavelength, but simultaneously also decreasing in amplitude. This is the exact opposite for the absorbance, which begins with low amplitude around 500nm and increases to a peak at 650nm. SC155 thermal paint changes colour from a light green to a very dark almost grey green. This colour change is demonstrated by the reflectance and absorbance results discussed as the lighter green colour is reflecting more light at 500nm (green light) than all other wavelengths before heating as opposed to after heating, when the sample absorbs the majority of all wavelengths. In the case of the SC 367 paint, the reflectance/absorbance spectrum demonstrates that the region from approximately 600 – 700 nm is reflected all other wavelengths before heating as opposed to after heating, when the sample absorbs the majority of all wavelengths. In the case of the SC 367 paint, the reflectance/absorbance spectrum begins to “flatten,” indicating the colour change to a shade of grey. The MC 165-2 paint follows a similar pattern, although reversed: where the SC 155 and 367 paints tend to “flatten”, the MC1665-2 paint initially increases in the

Figure 15. Ansys solution of transient heating for a) mild steel plates and b) KBr Disc for a range of temperatures.
percentage of absorbed source light, up until the first change of colour has been completed, and then the percentage of the absorbed light decreases. This is shown in figure 16.

Figure 16. Reflectance (left column) and absorbance (right) for SC155 (top) SC367 (middle) and MC165-2 (bottom).
The data for the reflectance of the SC155 can be displayed in a different way. Taking the location of the peak amplitudes as a co-ordinate point, (wavelength, amplitude) this can be plotted for the different temperatures for the SC155. Figure 17 shows the peak amplitude and wavelength vs. temperature with the colour changes shown below the graph. The advantage of this graph is that it shows very acutely the change in colour at the specified temperature for a particular paint and also shows simultaneously the percentage of reflected light as the paint varies with temperature. Thus for a MC paint, this could easily demonstrate the exact temperatures the colour changes occur at, with respect to the peak reflected wavelength. However, there is still far more information contained within the full spectra results.

D. Fourier Transform Infrared Spectrometry

The FTIR spectrometer requires modulation of the wavelength from the infrared source. This is done using an interferometer. The FTIR spectrometer also requires a detector to measure the intensity as a function of wavelength of the transmitted light once it has passed through the sample. Using Fourier transforms, a computer can analyse the signal received from the detector and display a single-beam infrared spectrum with intensity (a percentage of the light transmitted) vs. wave number (cm$^{-1}$). The spectrum displayed is characteristic to the coating and material being analysed and often called its “fingerprint.”

The FTIR spectrometer produces a spectrum as shown in figure 18. This shows the wavelengths that the sample absorbs the infrared laser which correlates to a specific chemical species. This information is useful to compare the results of the reflectance spectrum to the FTIR spectrum at the temperatures the samples were heated at. The full results of all paint types at all temperatures are attached in Appendix C.

However, due to time constraints the author has not yet been able to identify what the wavelengths correlate to in terms of specific chemical species. Therefore a relationship between the colour and the chemical composition is yet to be found. To identify the differences between the paints that were heated to different temperatures could be useful, without knowing what compounds or elements they represent. The fingerprint of
the chemistry-temperature relationship could be used in future studies to determine a desired outcome of a colour-chemistry-temperature-time relationship.

Figure 18. FTIR Spectrometer Results of MC 165-2

X. Conclusion

This report has covered literature regarding previous calibration methods for thermally sensitive paints. The current method of determining the temperature post test flight by hypersonic vehicles is to compare the post flight colour of the thermal paint to colour maps that have been produced by previous studies and from the manufacturer of the thermal paint. The results can become difficult to interpret as the final colour could indicate a false peak temperature or give an ambiguous temperature reading. The aim of this project was to explore a possible relationship between the colour and chemistry of thermal paints. This report has detailed the four major experiment processes used to attempt to establish this relationship.

The first experiment after the samples were prepared found that Cl and Si are present in the majority of the 15 types of paint tested under XRF spectrometry and determined that Cl and Si (separately or together) act as the resin in the majority of thermal paints. This experiment also found the element composition for all 15 paints. The full results for all 15 paints as stated earlier have been collated in to Appendix A for future studies in this field of research.

The computer analysis using Ansys was the second experiment undertaken as part of this project. The importance of this process cannot be understated as the soak times for a sample material need to be established so that good data can be collected accurately and succinctly. This process will need to be repeated should different sample materials need to be used in the future.

The third and fourth processes where conducted simultaneously once the samples had been prepared and heated. Reflectance spectroscopy as stated was used to give an accurate and unrefusable indication of true colour, this process is valuable in this study because it is not open to individual human interpretation, unlike RGB or HSV would have been. The data presented as a result of this process presents an easy visual way to interpret the reflected light as the paint is heated and the data can then be manipulated easily to represent the temperature point at which a specific paint completes a colour change.

Lastly, FTIR spectrometry gives a basic indication that there is a chemical reaction occurring as the paint changes colour as a result of temperature, although further analysis of the results needs to be done to determine
which species within the paint release the ligands which change the chemical composition and result in a colour change. Processes three and four in future studies of this subject will be capable of indicating not only the exact colour at the temperature change but in the event of a non colour change the specific chemical composition at a set temperature and thus the thermal paints can be used more accurately to determine dynamic temperature changes.

XI. Recommendations

The understanding of how permanent change thermal paints change colour is vital to accurately conduct temperature analysis of hypersonic vehicles after flight tests. This study was conducted for the purpose of gaining a greater understanding of the chemical reaction that occurs while undergoing a colour change while under steady state heating. The information provided will be used to assist further research in this field and hopefully lead to experimentation of the colour-chemistry-temperature-time relationship (transient heating simulations).

Further work is needed to examine the fundamental chemical reactions that the paints experience during heating and carefully measure the reaction rates and activation energies. It is suggested that the XRF analysis be done at each stage of the heating to see if the percentage by mass of the elements changes when heat is applied.

The relationship between colour and chemistry could be further examined while under transient heating to determine if a large enough amount of the chemical reaction takes place in short time periods to determine a temperature change.

It is anticipated that a full chemical analysis of the paints will be lead to a greater understanding of the mechanisms governing the paint colour, as well as eventually the time dependent behaviour of the paints.
Acknowledgements

The author would firstly like to thank Dr. Andrew Neely for his extreme patience, without which completion of this project would not have been possible. Thanks also to Associate Professor Hans Riesen for all his help and advice with this project and allowing the author to use several of the machines owned by the School of Chemistry.

A very special thank you also goes to Mr. Marcos de Almeida and Mr. Stuart Gay for all of their much needed technical assistance and practical knowledge. The author is also grateful for the help of Mr. David Sharp and Mr. Jim Baxter for assistance with the use of the Civil Engineering ovens.

The author would also like to thank Rishabh Choudhury for his assistance with the experiments and Derryn Knife and Wes Barlett for all of their assistance with regards to all work through this trying year, without whom, the author would never have made it. The author would finally like to thank all her friends and family for their continued support and having faith in the author for the completion of this project.
References


Paint, Software Package, Ver. 6.0, Microsoft® Windows®, Hewlett-Packard, United States, 2007


Tracy, P.J., “Investigation/Calibration of Temperature-Indicating-Paints for Potential Use in Scramjet Flight Tests” Final Project, ZACM 3851 Bachelor of Technology in Aviation, UNSW@ADFA, March, 2006


24