Design, Development and Construction of an ATEX Compliant ISO 9001:2008 Magnetic Ink Manufacturing Facility

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Abstract

This Thesis charts the cradle-to-grave development of a chemical processing plant suitable for the manufacture of 160 tonnes *per annum* of magnetic ink, and the associated, in-line process, quality control and assurance methodologies, developing innovations for the printing industry. The work was undertaken through Knowledge Transfer Partnership number 9576 between BemroseBooth Paragon, Ltd. and The University of Hull.

First, the formulation of magnetic inks is described and characterized through a variety of physical and chemical measurements. The magnetic properties of the development inks are presented. Thirteen different ink formulations were developed during the course of this work, all of which are currently now available on the global market, being sold in four continents to, amongst others, the Rail Delivery Group (RDG, formerly ATOC), Régie-Autonome des Transports Parisiens (RATP), all operators for the French motorway tolls (Sanef, Vinci, ASF, *etc*.), New York Metropolitan and Casa da Moeda do Brasil (CMB).

The design of the manufacturing process, including safety, health and environment consideration, are outlined, with their realization within an ISO 9001:2008 quality management system. The process economics are rationalized and pre-project estimations are contrasted with actual costs.

Fast moving manufacturing environments always require the development of innovations to expand product ranges and resolve issues associated with limited reverse supply chains and complications in the use of manufactured product. A variety of problems are presented, with realized and pragmatic pathways to their solution given. In keeping with the spirit of environmental responsibility, innovations in the development of water-based magnetic inks are presented, and routes to their low cost, *in situ* process monitoring, presented.

Last, an entirely new electrochemical approach to the detection of security threats in a mass transit environment is illustrated to a proof-of-concept.

Acknowledgements

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Contents

Chapter 1 - Introduction

Bemrose Booth Paragon (BBP) is a key member within the Access Control and Traceability (Identification) Division of the Paragon Group (a leader in print and document creation that dates back over 120 years). The Paragon Group is a global organization with over 150 sites worldwide. Annual revenue is currently reported to be €650 million, amassed due to both organic growth, and a series of recent acquisitions that have more than doubled its size within the previous three years. The Group's Access Control and Traceability (Identification) Division contributes €200 million (31%) to the revenue figure. The separate legal entities within the division include Paragon Identification in France and Romania, BemroseBooth in the UK, and Magnadata in the US. The division has 400 employees overall, with wider Paragon employing over 3500 people [1].

Bemrose was originally established in 1826 as a railway timetables manufacturer. In subsequent years, a merger with Henry Booth, created Bemrose Booth Ltd. In 2010, Bemrose Booth became a part of the Paragon group, who together were two of the largest and most experienced providers of ticket and RFID solutions in the world, forming BemroseBooth Paragon. BemroseBooth Paragon is currently the largest UK supplier of car parking tickets with a significant portfolio of customers such as NCP. It is also the worldwide leader in the supply of tickets and cards to the mass transit market, serving customers across Europe, Australia, Asia, Africa and North America.

A major contract for BBP is within the production of magnetic tickets for Network Rail to use in every train station within the UK. Magnadata were instrumental in developing the first magnetic tickets for British Rail over 30 years ago through the development of an in-house coating facility and magnetic encoding department [2]. By 1988 BBP, as a competitor, to Magnadata also entered the production of tickets through coating and printing.

Whilst BBP had been applying magnetic inks and security inks as part of its manufacturing process for over 20 years prior to 2014, those had been procured through an external supply chain. BBP wished to develop an embedded capability of creating and manufacturing magnetic inks or other materials, which are applied using a print manufacturing process. The reason for this was primarily to take control of an at-risk reverse supply chain but also accrue further sales. The company had no internal experience or knowledge pertaining to the formulation or manufacturing of specialist coatings. BBP decided to acquire this knowledge and capability, and in doing so more generically would understand the science behind the specific relationships of a suspended particle material in a formulation, potentially opening further product development avenues, for example within the security inks sector.

The content of this thesis captures my work at BBP, on a journey to becoming one of the few UK manufacturers and suppliers of magnetic inks into the print industry through the design, development, construction and commissioning of a purpose built magnetic ink manufacturing plant, coupled with quality control and assurance, and research and development laboratories. The accuracy and precision applied to the characterisation and process control leaves BBP with the ability to manufacture a wide range of magnetic inks, designed to meet detailed specifications.

The project was executed in the guise of a Knowledge Transfer Partnership (KTP), a part government-funded scheme operated through Innovate UK that helps businesses to innovate and grow. Each KTP is a three-way partnership between a business, an academic institution and a graduate. The academic institution employs the recently-qualified graduate who works at the company. The graduate, known as the 'Associate', brings new skills and knowledge to the business.

The initial purpose of the project was to internalize the manufacture of magnetic inks at BemroseBooth Paragon (BBP), Hull. Secondly, a water-based (water containing) formulation was targeted for the same application, but with an aim to remove the aggressive, environmentally unfriendly solvents.

The project was carried out by first characterising competitor magnetic ink samples through physicochemical and magnetic analysis. This characterisation process occurred in tandem with the design and construction of the manufacturing facility, so that once characterised, the products could be trial-manufactured at a small scale, and fully scaled-up to ensure product functionality before switching from the existing suppliers.

The ink manufacturing facility was a huge success, with BBP having developed high quality product and obtaining customer confidence. The ink and printed goods are now manufactured and sold to markets in the UK (ATOC National Rail and Virgin Trains, London Underground, Nexus, Mersey Rail, RAM Systems), Ireland (Irish Rail), France (motorway tolls and Paris Métropolitain), Poland (Hegard), USA (New York Metro, Phoenix trains), Africa (Cairo Métro) and South America (Caracas, Casa da Moeda do Brasil). Paragon Group is now the largest producer of magnetic ink in Europe (over 160 tonnes per annum). This has indirectly led to a tripling of the business turnover for BBP (from £8M to £24M per annum).

This thesis first introduces magnetic properties of solids, and examines their deployment for magnetic tickets. Subsequently, the routes to manufacture and commercialization are considered.

References

[1] http://www.printweek.com/print-week/news/1153043/paragon-group-confirms-magnadata-acquisition - Accessed 02/06/2016
[2] http://www.magnadata.co.uk/index.php/products/magnetic-ticket-leaders - Accessed 03/06/2016

Chapter 2 – Magnetism, Magnetic Inks and Printing Methodologies

2.1 Magnetism

Magnetism is one of the fundamental forces of the universe alongside atomic forces and gravity. Magnetic and electrical fields are related in their behaviour. The lines of a magnetic field exit the magnet from the north pole and re-enter at the south pole. Magnets can be permanent or temporary (hard or soft). Permanent magnets constantly produce a magnetic field, whereas temporary magnets produce a field in the presence of another magnetic field, and retain it for some time afterwards. An electromagnet produces a field only when electricity travels through the wire coils.

Typically magnets are made from metal or alloy. Types include; ceramic (weak), AlNiCo (medium strength), Neodymium (strong) or Samarium (very strong). Flexible plastic magnets are also in development but are currently weak and not operable under ‘normal’ conditions. The magnets used to orientate products such as magnetic ink during a coating process are of NeFeB (neodymium iron boron) composition [1].

The above materials are not naturally occurring and must be processed into magnets, this is completed through the use of magnetic domains (in the structure of ferromagnetic materials). Each domain is essentially a magnet with a north and south pole. In an un-magnetized ferromagnetic system all of the north poles point in random directions with no net force. In a magnet these domains are all aligned in the same direction, and the larger the quantity that point in the same direction, the stronger the magnet (due to the north of one microscopic domain entering the south of the next). Exposure to a magnetic field, physical hammering or an electric current can further encourage alignment of magnetic domains.

When aligning with a magnetic field, there is a slight delay between application of field and change in domain. This is known as hysteresis and occurs as the domains move and align. The resultant strength is related to the amount of force required to move the domains. The permanence (retentivity) depends on the difficulty to encourage alignment. Materials that are harder to magnetize often retain magnetization for longer periods, while those that magnetize easily can revert. A magnet can be fully demagnetized by a field aligned in an opposite direction, or by heating above the Curie point.

Moving electrical charges are responsible for magnetic fields in permanent and electromagnets. For an electromagnet, a flow of electrons provides the movement for the field alignment, whereas in a permanent magnet the electrons of the fixed metal atoms provide the field. Generally electrons exist in the orbital in pairs (opposite spins). Ferromagnetic elements have several unpaired electrons in the same spin. Iron has four unpaired electrons with the same spin, forming an orbital magnetic moment. This moment is a vector as it has magnitude and direction (related to field strength and torque). A whole magnet's magnetic moment is the sum of all moments. This behaviour of the atoms encourages the alignment of the poles of all atoms. During the formation of the metal the molten material cools and the crystalline atoms align parallel to those with the same spin. This gives rise to domains within the magnet, and therefore the randomized direction of the domains making up the magnet material. Magnets attract materials that have unpaired electrons that spin in the same direction [2].

2.2 Solvent Based Magnetic Ink Systems

Magnetic thin film coatings are typically manufactured using magnetic pigments such as maghemite or magnetite (Fe_2O_3 or Fe_3O_4). The dispersion of this pigment is performed in a wet-milling process for a sufficient period to break down agglomerations of magnetic particles. The aim is to coat each single pigment particle in surfactant and binder. Dispersion quality within the resin solution determines the quality of the coating and can be measured in relation to surface smoothness, orientation ratio, signal-to-noise ratio, off-track performance, modulation noise, coercive force and also wear properties.

Iron oxides (maghemite/magnetite for example) are 'softer' ferrites, present in the manufacture of low coercivity products. Magnetite is of the inverse spinel structure with a general form ($Fe^{II}Fe^{III}{}_2O_4$), it possesses a cubic close packed structure in which half of the Fe^{III} occupy the tetrahedral holes, the Fe^{II} and the other half of the Fe^{III} are embedded within the octahedral holes. See figure 2.1 for a diagram of the structure.

Figure 2.1: Inverse spinel cubic close packed structure of magnetite [3].

Advanced understanding of inverse spinel structures explains that Fe^{3+} has five unpaired 3d electrons within a high spin octahedral/tetrahedral ligand field. Fe^{2+} has four unpaired 3d electrons within a high spin octahedral field. All the (Fe^{3+} and Fe^{2+}) unpaired electrons in the octahedral sites are magnetically coupled in parallel to afford a ferromagnetic sublattice. The spins of each sublattice are anti-parallel to one another. This is due to the unequal distribution of unpaired electrons within both magnetic sublattices that the two sublattices do not mutually compensate, therefore giving rise to ferrimagnetism.

Maghemite however possesses a cubic lattice of oxygen with Fe^{III} randomly distributed amongst tetrahedral holes (See figure 2.2 below).

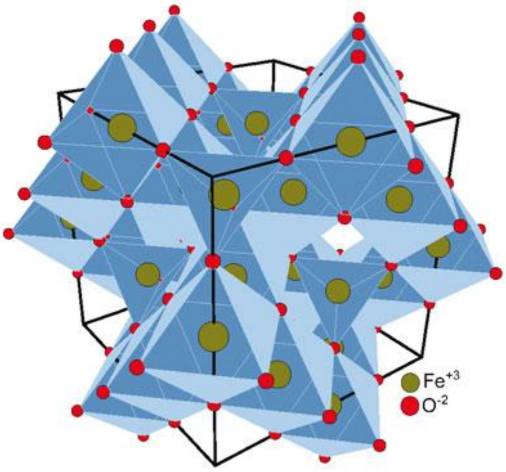


Figure 2.2: Structure of maghemite [4].

The above structures afford acicular (‘needle’) shaped particles possessing ferrimagnetic interactions which allow for magnetization of the system to occur. In this compound, coercivity is entirely controlled by particle elongation (particles are typically between 0.4 and 0.8 µm with an aspect ratio of between 6:1 and 12:1).

2.3 Magnetic Ink formulation

2.3.1 How is magnetic ink made?

High quality coatings are characterized by a perfect pigment dispersion, optimal pigment particle size, and long-term stabilization of the dispersed particles in the formulation.

The dispersion of the pigment in magnetic inks to form stable suspensions can be divided into wetting, dispersion and stabilization. They are represented diagrammatically in figure 2.3.

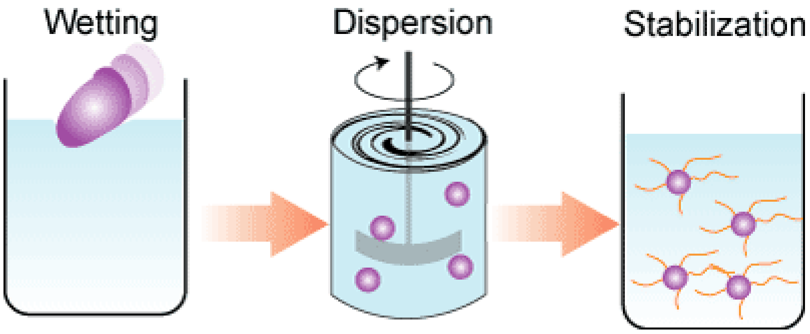


Figure 2.3: The process of dispersion [5].

2.3.2 Pigment Wetting, Grinding and Stabilization

The moisture and air are displaced from the surface and between the particles of the iron oxide pigment aggregates and agglomerates and is replaced by the carrier/solvent; the solid/gaseous interface is converted into a solid/liquid interface.

Through shear and impact forces (mechanical energy exerted by the ball mill attritors), the pigment agglomerates are separated into smaller units and dispersed until uniform. Left in this state, flocculation would occur due to the magnetic nature of the particles. The particles are stabilized by dispersing/wetting agents in order to prevent this. The resultant suspension is ultimately stabilized due to the adsorption of binder molecules at the pigment surface.

2.3.3 Wetting

Adsorbed materials on the surface of the pigments and inside the agglomerates such as water, oxygen, air, and/or other media in the process must be replaced by the solvent/carrier. Full wetting out of the primary sized pigment particle helps to enhance the technical performance and functionality of the magnetic coating. Dispersing additives facilitate liquid/solid interfacial interactions by removing the air/solid interface – see figure 2.4.

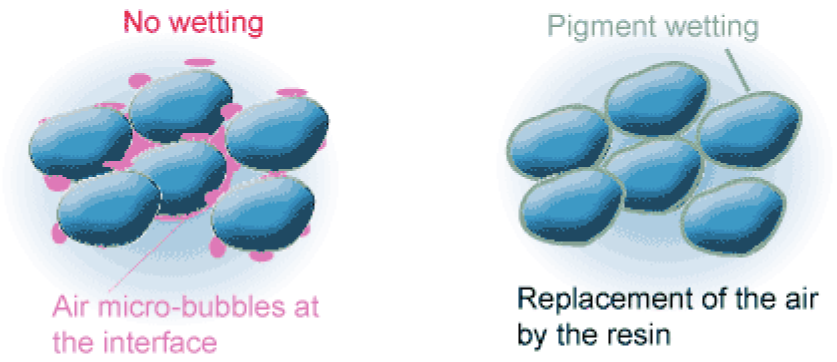


Figure 2.4: Displacement of air by solvent [5].

The efficiency of the wetting is related to the surface tension properties of the solvent and the pigment, as well as the resultant viscosity.

Spontaneous wetting processes are driven by the minimization of free surface energy. Forced wetting processes need external force to be applies however spontaneous de-wetting will take place when the force is no longer present. The thermodynamic conditions for wetting require the work of liquid/solid adhesion (W_a) to be as high as possible and, for unlimited wetting, at least more than half of the work of cohesion (W_k). Velocity of penetration of a liquid into a powder is quantified by the Washburn equation (Equation 2.1) [5]:

$$V = \frac{dh}{dt} = \frac{r\sigma Cos\theta}{C^2 \cdot 2\eta h} = \frac{r}{C^2} \cdot \frac{W}{2\eta h} \qquad \text{Eq 2.1}$$

The terms are defined as:

h - depth of penetration
t - time
σ - surface tension of the wetting liquid
η - viscosity
θ - wetting angle
r – mean radius of capillaries
C - structural coefficient, associated with parameters of the porous structure
W - energy (heat) of wetting.

The wetting step of dispersing processes is enhanced through the use of wetting agents and/or binders with a lower surface tension/viscosity.

Following the commencement of the wetting stage, the de-agglomeration of the pigment particles must take place and is generally achieved through mechanical action provided by high impact mill equipment (Figure 2.5). During milling the cohesive forces inside the agglomerates need to be overhauled. Energy is added to the system and therefore smaller particles result, thereby effecting loosened inter-particle contact durability. The action of shear stresses can then more easily destroy pigment clusters [5].

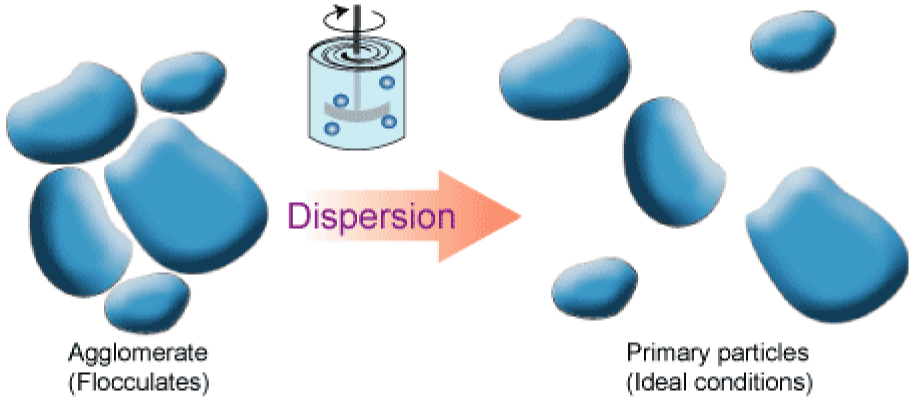


Figure 2.5: Pigment dispersing [5].

As the pigment powder is reduced to individual particles, higher surface areas become exposed to the solvent/vehicle and newly formed surfaces need to be wetted out by higher amounts of additives.

Once dispersed, flocculation tends to occur. From a structural perspective, the aggregates are similar to the agglomerates however the interstitial spaces in the pigments are solvent/resin solution rather than air. The grinding process actions de-flocculation, counteracting this process, however if stabilizing agents are not incorporated in the formulation then the functionality of the magnetic ink may be reduced, and changes in rheology of the system encountered.

2.3.4 Stabilization

The aim of stabilization is to keep the pigment particles fully separated as achieved in the wetting step, but also to control the degree of pigment particle size through the let-down and filling phase, storage and in coating

.

Flocculated pigment suspensions result in poor rheology and low storage stability. They are characterized by the non-uniform spatial distribution of particles, facilitating immediate interparticle contact.

Well-dispersed but unstabilized fine particle size magnetic pigment suspensions can easily be ruined by letting down into an inadequate base. Flocculation typically breaks down when shear is applied but re-occurs when the shear is removed. To mitigate, immediately after grinding pigment suspensions must be stabilized by additives, as seen in figure 2.6.

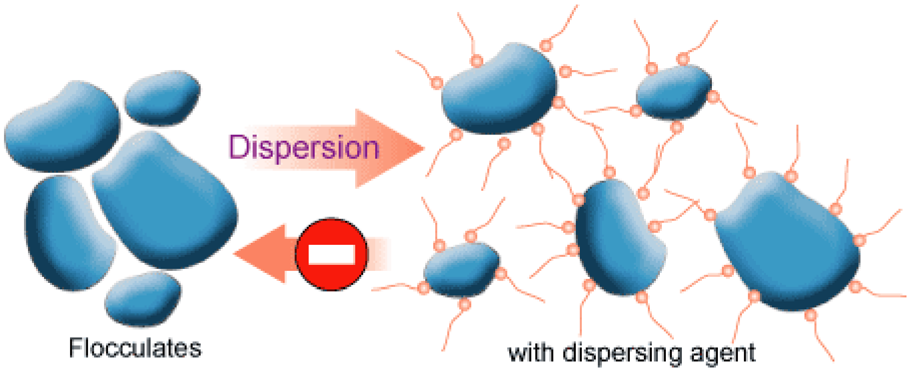


Figure 2.6: Dispersing agents avoid flocculation [5].

Stabilization is achieved through the absorption of stabilizing molecules onto the surface of the pigment particles. Their repulsive forces prevent other particles from reaching a distance whereby van der Waals forces are able to cause flocculation.

Pigmented dispersions can be stabilised through steric or electrostatic methods. Pigment particles are sterically stabilized when the surface of the solid particles are completely covered by polymers, removing the possibility of physical particle-to-particle contact. Strong interactions between polymers and solvents prevent the polymers from contact with each other. Electrostatic stabilization takes place when equally-charged local sites on the pigment surface come into contact with one another. Particles of the same charge repel, and the Coulomb-repulsion of the charged particles encourages stability [5].

The pigment particles in the formulation carry electrical charges on their surfaces. Through the use of additives the number of charges can be increased to make all pigment particles equally charged. Effectively, a charge is generated on the pigment surface, and a more diffuse cloud of oppositely charged ions develops around it. As two particles approach the charge effectively provides a barrier to closer particle interactions. Stabilization increases as the thickness of the layer increases. See an example of the system in figure 2.7.

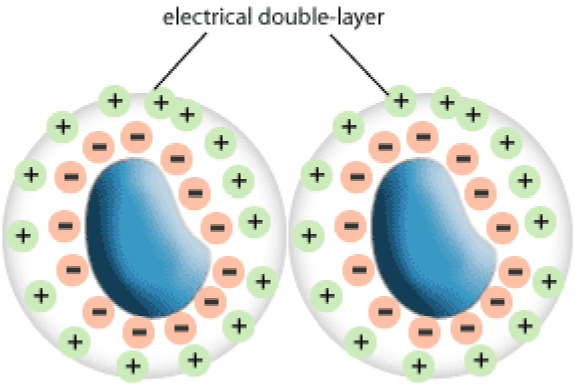


Figure 2.7: Electrostatic stabilization [5].

The additives selected for dispersions are polyelectrolytes - high molecular weight products which contain a multitude of electrical charges in the side chains.

Polycarboxylic acid derivatives are also used as polyelectrolytes in the coatings industry. The polyelectrolytes adsorb onto the pigment surface and transfer their charge to the pigment particle. Through electrostatic repulsion between equally charged pigments, the de-flocculated state becomes stabilised. Commonly a combination of electrostatic charges and steric stabilisation work most effectively in the same formulation.

Charge stabilization is not the most effective in formulations with low dielectric constant (most organic solvents and plasticisers), and steric stabilization is required to maintain dispersion. Steric stabilization employs the adsorption of a layer of resin or polymer chains on the surface of the pigment. As pigment particles approach each other, these adsorbed polymeric chains intertwine, and in so doing they lose a degree of freedom. This loss of freedom is expressed, in thermodynamic terms, as a reduction in entropy, which is unfavourable and provides the necessary barrier to prevent further attraction. As the chains intermingle, solvent is forced out from between particles. This leads to an imbalance in solvent concentration which is resisted by osmotic pressure tending to force solvent back between the particles, thus maintaining their separation (figure 2.8).

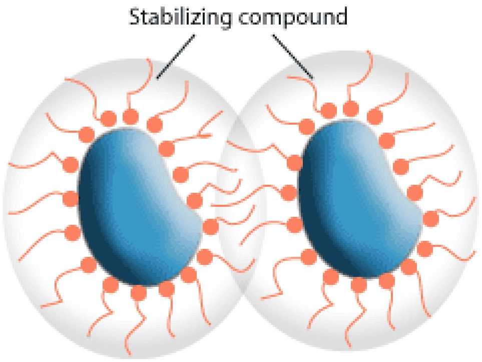


Figure 2.8: Steric stabilization [5].

One fundamental requirement of steric stabilization is that the chains are fully solvated by the medium. This means the chains will be free to extend into the medium, and possess the aforementioned freedom, so that the solvent needs to solubilise the polymer chain for the polymer chain. In systems where the chains are not so well solvated they will prefer to lie next to each other on the surface of the pigment, providing a very much smaller barrier to inter-particulate attraction.

The greater steric repulsion generated by the addition of polymeric dispersants moves the minimum in the potential energy curve, and thus reduces the overall viscosity (see figure 2.9).

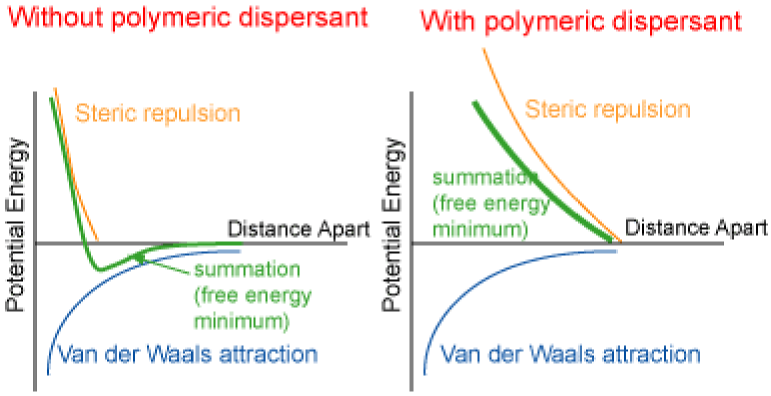


Figure 2.9: Potential Energy curves [5].

This stabilization mechanism occurs in solvent- based systems and in water-reducible systems which contain solvated resins. Through specific structural elements composed of pigment affinic groups (polar) and resin-compatible chains (non-polar), these dispersing agents exhibit definitive surface-active properties. In other words, they not only stabilize the pigment dispersion, but they also function as wetting additives [5].

2.4 Magnetic Ink at Bemrose Booth Paragon

BBP now manufacture two main types of magnetic ink; high coercivity and low coercivity (HiCo and LoCo). Magnetic ink can be manufactured through the processing of magnetic pigments which are classified as soft or hard magnetic materials (iron oxides and ferrites respectively). They exhibit ferrimagnetic properties and can be encoded to store binary information.

The main difference between HiCo and LoCo inks is how difficult they are to encode and erase the information on each type of ink. High Coercivity or "HiCo" inks are recommended for the majority of applications. HiCo inks are typically a reddish-purple in colour and are encoded with a stronger magnetic field (2750 or 3500 Oersted). The stronger magnetic field makes HiCo inks more durable because the data encoded within is less likely to be unintentionally erased when exposed to an external magnetic field. HiCo inks are common in applications where they require a longer card life *i.e.* credit cards, bank cards, access control cards *etc*. [6].

Low Coercivity or "LoCo" inks are good for short term applications. LoCo magnetic inks are generally brown or black in colour and are encoded with a low intensity magnetic field (300 Oersted). LoCo inks are typically used for travel tickets including rail tickets and products such as hotel room keys and season passes for theme parks, amusement parks *etc.* [6].

Magnetic inks are manufactured to exact and detailed formulations; each ink type has a unique formulation process as there are many factors to consider, some of which include viscosity and drying efficiency. These individual properties are achieved by fine-tuning the chemical composition and manufacturing process.

The key factor in the magnetic ink manufacture process is the dispersion of the ferrimagnetic particles. It is these particles which enable the ink to be magnetised and as such hold the binary information. Most inorganic pigments require special milling techniques to produce sub-mm sized particles for stable dispersion [7].

The easiest and most effective method of milling particles to the required state is through the use of a batch attritor or “S-type” attritor, also known as a ball mill. The batch attritor is the simplest to use, with no pre-mixing required and all material components able to be loaded directly into the tank. The grinding media are then agitated by a shaft with arms, rotating at high speed. See figure 10 for a diagrammatic representation of its operation. This motion causes the media to exert both shearing and impact forces on the material, resulting in optimum size reduction and particle dispersion. The attritor is equipped with a diaphragm pumping system, which recirculates the product from the base to the top of the vessel during grinding. The pump is also used for discharging the final product by a diversion through valves.

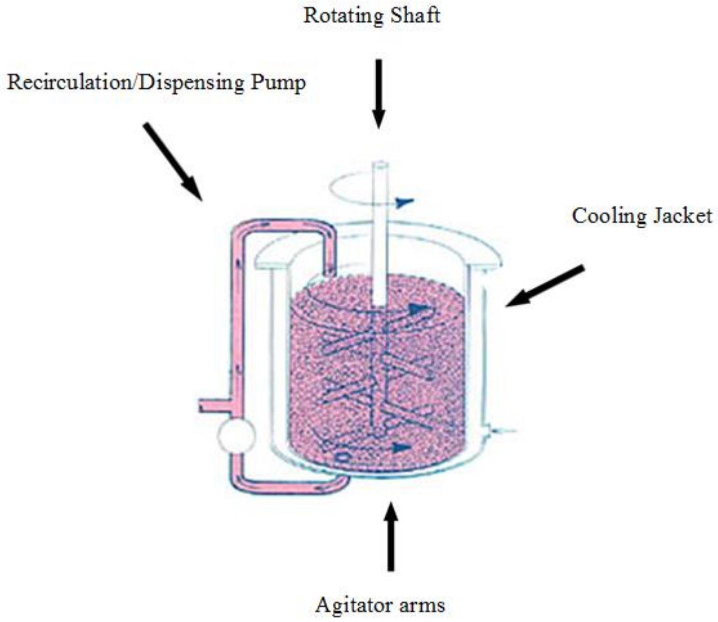


Figure 2.10: Batch Attritor [8].

The temperature of the magnetic ink can be stabilised and alternated through the use of a water jacketed tank as seen in figure 2.10 above. It is observed that the grinding media itself is affected by the milling/grinding process, resulting in a size reduction in media over time. The consequence of this is a reduction in the effectiveness of the milling process and also fragments of the media entering into the ink formulation. The fragmentation issue is eradicated through the use of five or ten-micron filters upon product discharge.

In order to create a homogenous magnetic ink formulation, further chemicals are added to the magnetic pigment during the milling process. Dispersants or “wetting agents” are added to the grinding media along with the required solvent volume, and dependant on application, suspending agents and head cleaners. Dispersants stabilise the pigment particles by lowering the mechanical energy required for grinding. Wetting agents are selected based on chemical suitability within the formulation. Suspending agents act as a holding material, enabling an even distribution of components throughout the mixture, and reducing settling velocity. Head cleaner is used to induce an abrasive nature to the surface of the magnetic stripe in the dried product, thereby maintaining a clean read/write head within the ticket reading machine.

Once the raw materials have been subjected to the attrition stage and have passed the quality control tests (particularly dispersion through microscopic analysis), a resin solution is added to the mixture. Occasionally the resin is added before the pigment, but this is dependent on final product specification. The resin has binding properties, holding the ink within its boundaries, encouraging homogeneity and enabling an adhesion to the substrate. If required, a plasticiser is incorporated, which allows the ink to be flexible once dried.

The standard formulation for the production of the UK rail (Hull) LoCo magnetic ink contains six key components described as follows:

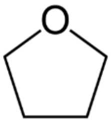
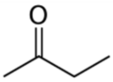
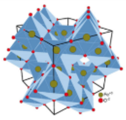
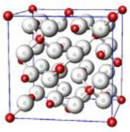
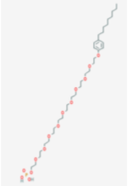
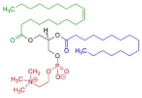
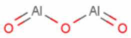
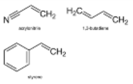
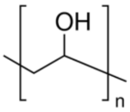
1. **Solvent** – This is the carrier that enables the processing of the formulation and initial wetting of the pigment.
2. **Binder** – This reduces the mechanical grinding force applied to the pigment particles at the start of manufacture, so that pigment particles do not become integrally damaged.

3. **Wetting Agent** – This creates a homogenous environment by chemically binding to the pigment surface to facilitate equal dispersion of all particles and prevents flocculation post dispersion.
4. **Pigment** – The pigment provides the functionality for the ink as it supplies the magnetic properties required. It is also the main source of final product colour.
5. **Resin** – This provides the adhesive properties of the slurry ensuring that the slurry adheres to the required substrate by binding and 'wrapping' around the dispersed particles to aid with dispersion.
6. **Head Cleaner** – This creates an abrasive surface on the dried ink as it passes through the reader machine which ensures the read/write head remains clear and prevents blockage.

The manufacture of the UK Rail product contains the following specific components (these are expanded in Table 2.1 for Hull LoCo:

- **MEK** – Solvent
- **PVA/PVC/PVOH** – Resin component
- **Rhodafac RE/610E** – Wetting Agent
- **Lecithin** – Wetting Agent
- **Alumina** – Head Cleaner
- **Magnetite –** Pigment
- **Maghemite** – Pigment
- **Resin** – Contains resin components and plasticizer.

Table 2.1: Hull LoCo Formulation Components:

Material	**Description**	**Alternate Names**	**Chemical Structure**	**Photograph (a)**	**Hazards**	**PPE**
Tetrahydrofuran	Solvent	Butylene Oxide				
Methyl Ethyl Ketone	Solvent	Butanone				
Iron (III) Oxide	Pigment	Maghemite			None	
Iron (II,III) Oxide	Pigment	Magnetite				
Rhodafac RE-610/E	Wetting Agent	Polyoxyethylene nonylphenyl ether				
Metarin P	Wetting Agent	Lecithin			None	
Alumina E330	Headcleaner	Aluminum Oxide			None	
Nipol 1432	Resin Component	ABS Rubber			None	
UAGH-1	Resin Component	Hydroxyl modified polyvinyl acetate/chloride/ alcohol			None	

a) Images taken from a diversity of sources available on the worldwide web.

The standard formulation for the production of a mainstream HiCo magnetic ink such as the New York Metro formulation contains six key components, indicated below:

1. **Solvent** – This provides a carrier for all components to move through and enables initial pigment wetting.
2. **Suspending Agent** – This reduces the settling velocity of the dense HiCo pigment particles ensuring an even distribution through the slurry.
3. **Wetting Agent** – This creates a homogenous environment allowing for equal dispersion of all particles throughout the slurry and prevents clumping.
4. **Pigment** – The pigment provides the functionality of the slurry as it supplies the magnetic properties required along with adding the required colouration.
5. **Resin** – This provides the adhesive properties of the slurry ensuring that the slurry adheres to the required substrate by binding and wrapping around the dispersed particles.

The liquid carrier often used is a non-aqueous solvent like a non-polar organic solvent, but aqueous solvent can be also used.

Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. The suitable organic surfactants and carrier liquids are important factors that can affect the stability of magnetic fluids. Surface coating can restrict the agglomeration and improve the dispersibility of the Fe_3O_4 and consequently, can improve the stability of the magnetic fluids largely.

A binder is a material (polymer or rubber) that holds or draws other materials together to form a cohesive whole mechanically, chemically, or as an adhesive. Liquid binders are added to a dry substance in order to draw it together in such a way that it maintains a uniform consistency. It helps to stick the solids onto the paper and also prevent the flocculation of particles.

Magnetic particle suspensions have been extensively studied due to their many practical applications, especially in the magnetic tape industry. Magnetic recording media, in general, consist of a coating of fine magnetic particles on a non-magnetic plastic substrate.

The manufacture of the Boston New York HiCo (a standard HiCo formulation) requires the following components:

- **MEK -** Solvent
- **Solsperse 24000 GR –** Wetting Agent
- **Bentone SD-2 –** Suspending Agent
- **Vulcan XC72 –** Pigment and antistatic agent
- **Barium Ferrite P2169 -** Pigment
- **Resin -** Resin

2.5 Magnetic Ink Coating

The magnetic ink coating machine in Hull operates *via* a gravity feed process whereby the ink is diluted with organic solvent to a viscosity between 2500 and 5000 cP and agitated until a homogenous mixture is formed, then is transferred into a holding pot above the substrate with fixed agitators.

The substrate carries a thermally activated verso surface and magnetic ink is applied to the non-thermal side. See figures 2.11 and 2.12 for substrate construction and specifications. The magnetic ink is deposited through 11 mm wide apertures before passing through a 4 kG poles-opposed magnet.

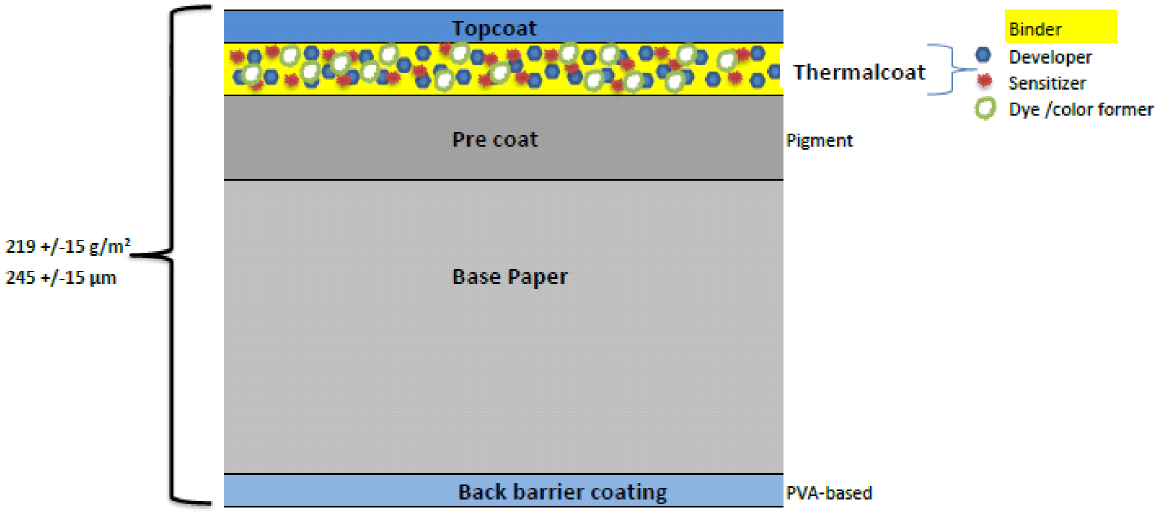
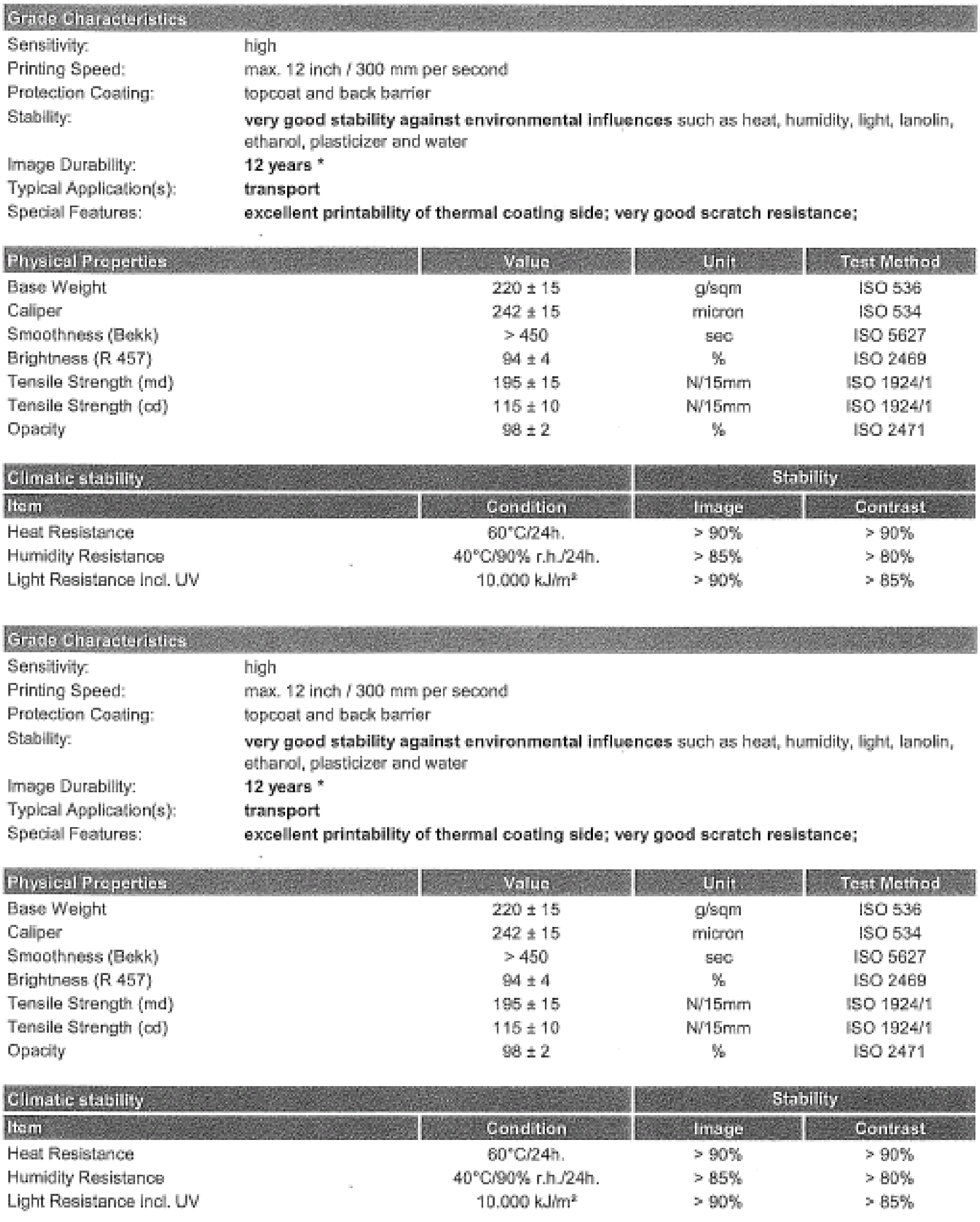


Figure 2.11: Thermal substrate construction [9]



Grade Characteristics	
Sensitivity:	high
Printing Speed:	max. 12 inch / 300 mm per second
Protection Coating:	topcoat and back barrier
Stability:	**very good stability against environmental influences** such as heat, humidity, light, lanolin, ethanol, plasticizer and water
Image Durability:	**12 years ***
Typical Application(s):	**transport**
Special Features:	**excellent printability of thermal coating side; very good scratch resistance;**

Physical Properties	Value	Unit	Test Method
Base Weight	220 ± 15	g/sqm	ISO 536
Caliper	242 ± 15	micron	ISO 534
Smoothness (Bekk)	> 450	sec	ISO 5627
Brightness (R 457)	94 ± 4	%	ISO 2469
Tensile Strength (md)	195 ± 15	N/15mm	ISO 1924/1
Tensile Strength (cd)	115 ± 10	N/15mm	ISO 1924/1
Opacity	98 ± 2	%	ISO 2471

Climatic stability		Stability	
Item	Condition	Image	Contrast
Heat Resistance	60°C/24h.	> 90%	> 90%
Humidity Resistance	40°C/90% r.h./24h.	> 85%	> 80%
Light Resistance Incl. UV	10.000 kJ/m²	> 90%	> 85%

Grade Characteristics	
Sensitivity:	high
Printing Speed:	max. 12 inch / 300 mm per second
Protection Coating:	topcoat and back barrier
Stability:	**very good stability against environmental influences** such as heat, humidity, light, lanolin, ethanol, plasticizer and water
Image Durability:	**12 years ***
Typical Application(s):	**transport**
Special Features:	**excellent printability of thermal coating side; very good scratch resistance;**

Physical Properties	Value	Unit	Test Method
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Tensile Strength (md)	195 ± 15	N/15mm	ISO 1924/1
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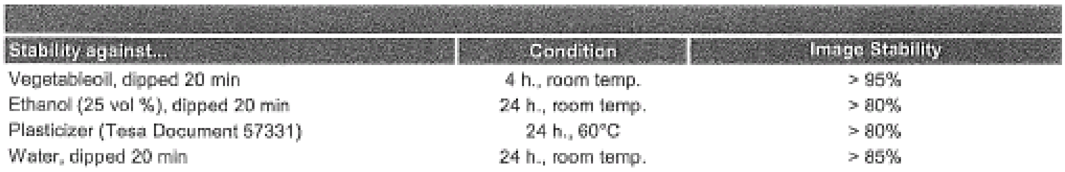
Climatic stability		Stability	
Item	Condition	Image	Contrast
Heat Resistance	60°C/24h.	> 90%	> 90%
Humidity Resistance	40°C/90% r.h./24h.	> 85%	> 80%
Light Resistance Incl. UV	10.000 kJ/m²	> 90%	> 85%



Stability against...	Condition	Image Stability
Vegetableoil, dipped 20 min	4 h., room temp.	> 95%
Ethanol (25 vol %), dipped 20 min	24 h., room temp.	> 80%
Plasticizer (Tesa Document 57331)	24 h., 60°C	> 80%
Water, dipped 20 min	24 h., room temp.	> 85%

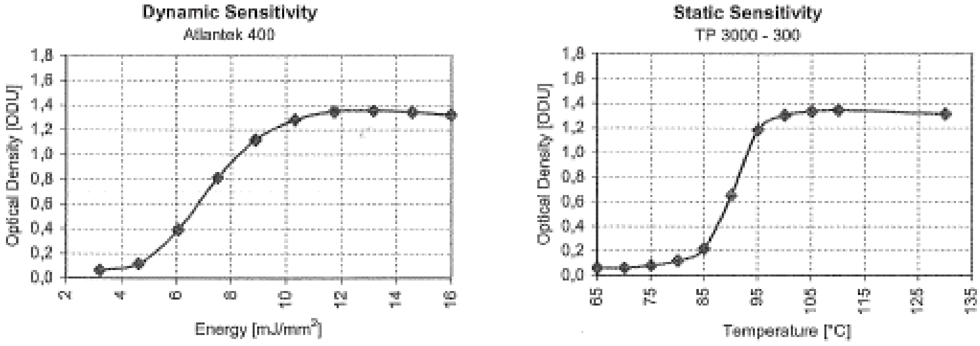
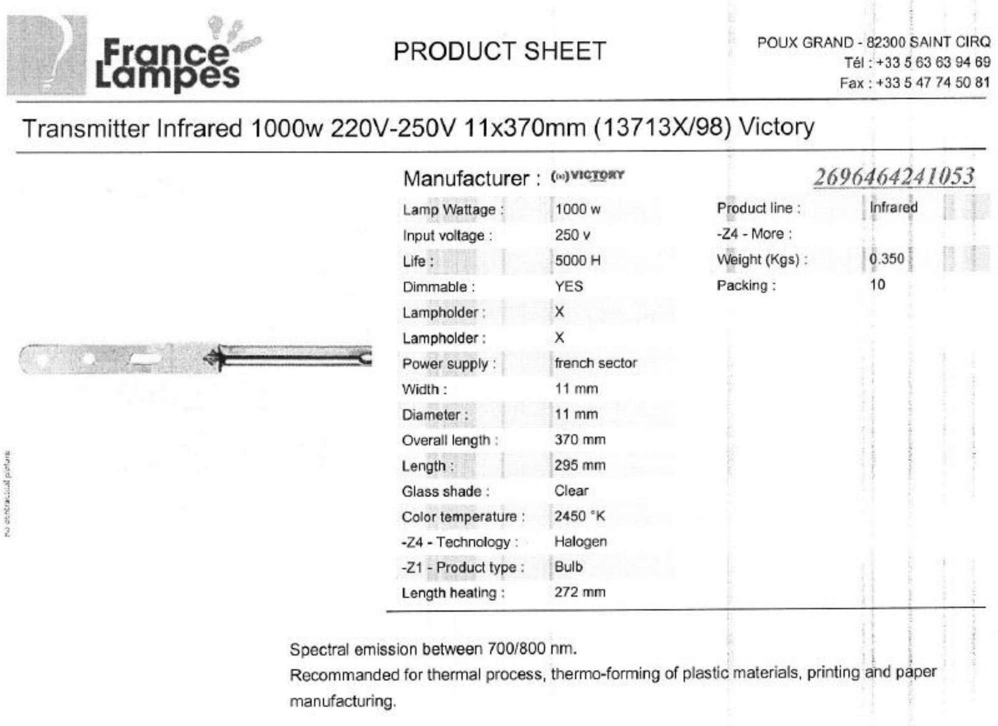


Figure 2.12: Specification for thermal substrate [9] (split over two pages).

The coating process is pictured in figures 2.13 to 2.18.

Figures 2.13 to 2.18: Photographs of the Magnacoater at BBP Hull.

Once the magnetic ink is applied to the substrate it passes through a 5 m Near Infrared drying oven at 60 m/min. Although the wavelength of the light (700-800 nm) is slightly smaller than that required for near-infrared (1-2.5 µm), the system dries the coated board sufficiently. The specification for the drying lamps is contained in figure 2.19.



France Lampes

PRODUCT SHEET

POUX GRAND - 82300 SAINT CIRQ
Tél : +33 5 63 63 94 69
Fax : +33 5 47 74 50 81

Transmitter Infrared 1000w 220V-250V 11x370mm (13713X/98) Victory

Manufacturer : VICTORY

2696464241053

Lamp Wattage :	1000 w	Product line :	Infrared
Input voltage :	250 v	-Z4 - More :	
Life :	5000 H	Weight (Kgs) :	0.350
Dimmable :	YES	Packing :	10
Lampholder :	X		
Lampholder :	X		
Power supply :	french sector		
Width :	11 mm		
Diameter :	11 mm		
Overall length :	370 mm		
Length :	295 mm		
Glass shade :	Clear		
Color temperature :	2450 °K		
-Z4 - Technology :	Halogen		
-Z1 - Product type :	Bulb		
Length heating :	272 mm		

Spectral emission between 700/800 nm.
Recommanded for thermal process, thermo-forming of plastic materials, printing and paper manufacturing.

Figure 2.19: Specification of lamps used in drying system on the Magnacoater [10].

Figures (2.20 to 2.32) show various information about the magnetically coated substrate using a variety of imaging techniques including surface profiling and scanning electron microscopy.

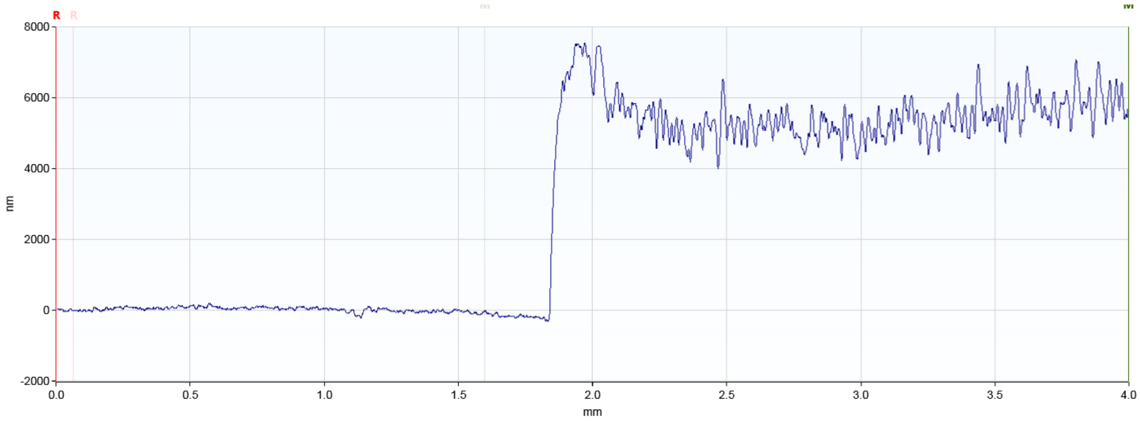


Figure 2.20: Dektak stylus profile of magnetic stripe (perpendicular to stripe).

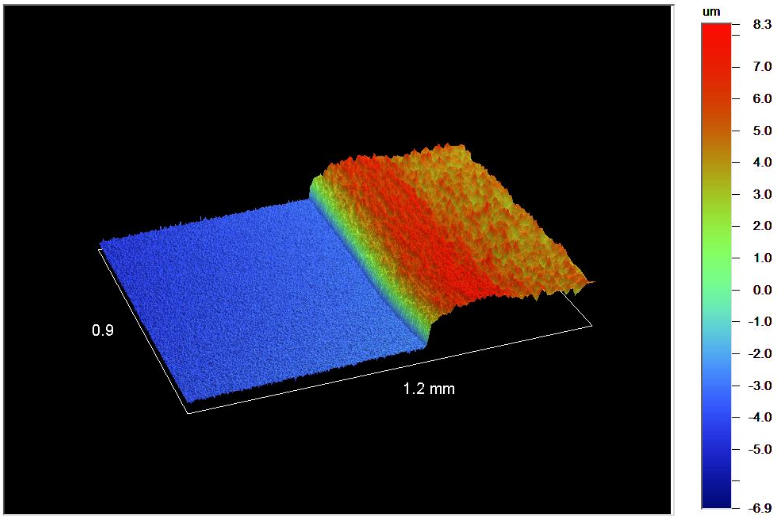
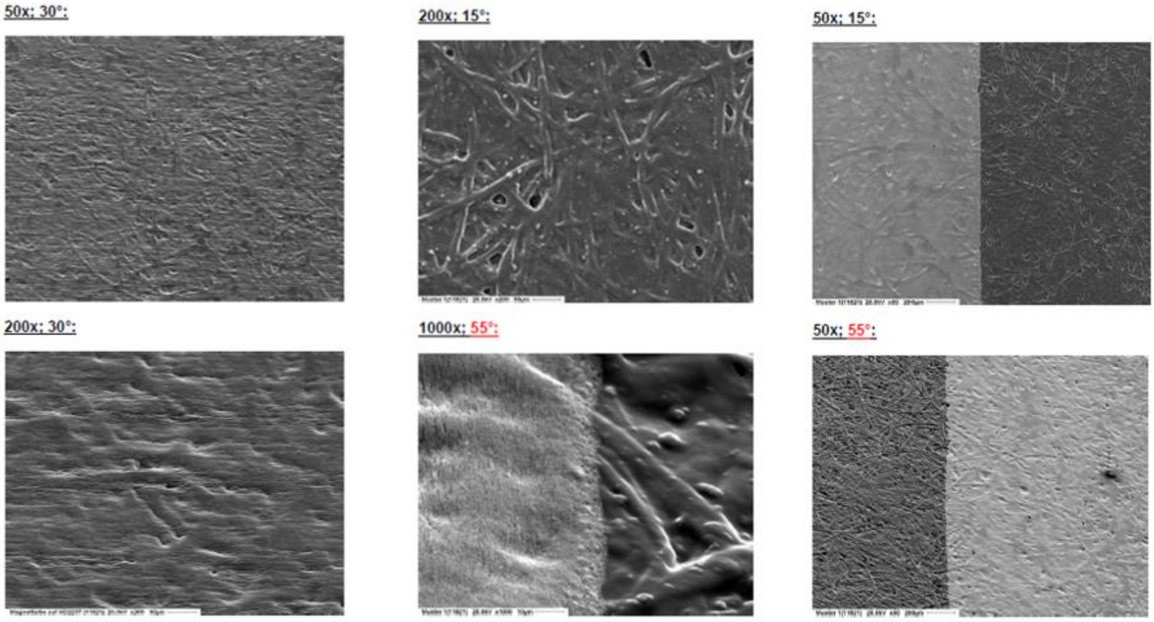
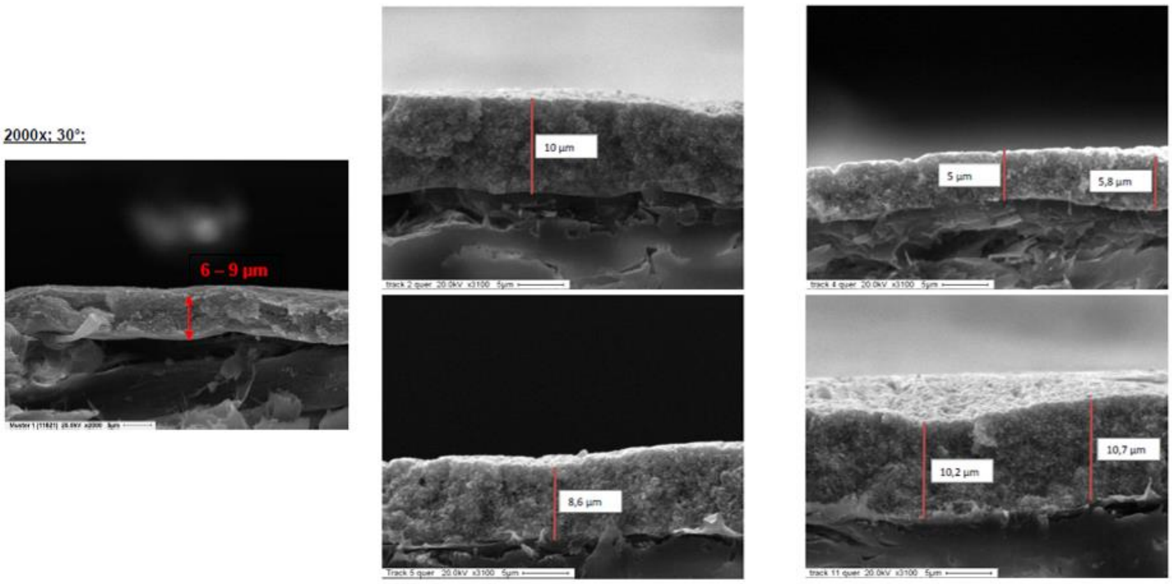


Figure 2.21: White Light Interferometer profile of magnetic stripe.


50x; 30°:
200x; 15°:
50x; 15°:
200x; 30°:
1000x; 55°:
50x; 55°:

Figures 2.22 to 2.26: Microscopy of magnetic stripe and substrate from vertical position [9].



Figures 2.27 to 2.31: Microscopy of magnetic stripe and substrate from horizontal position [9].

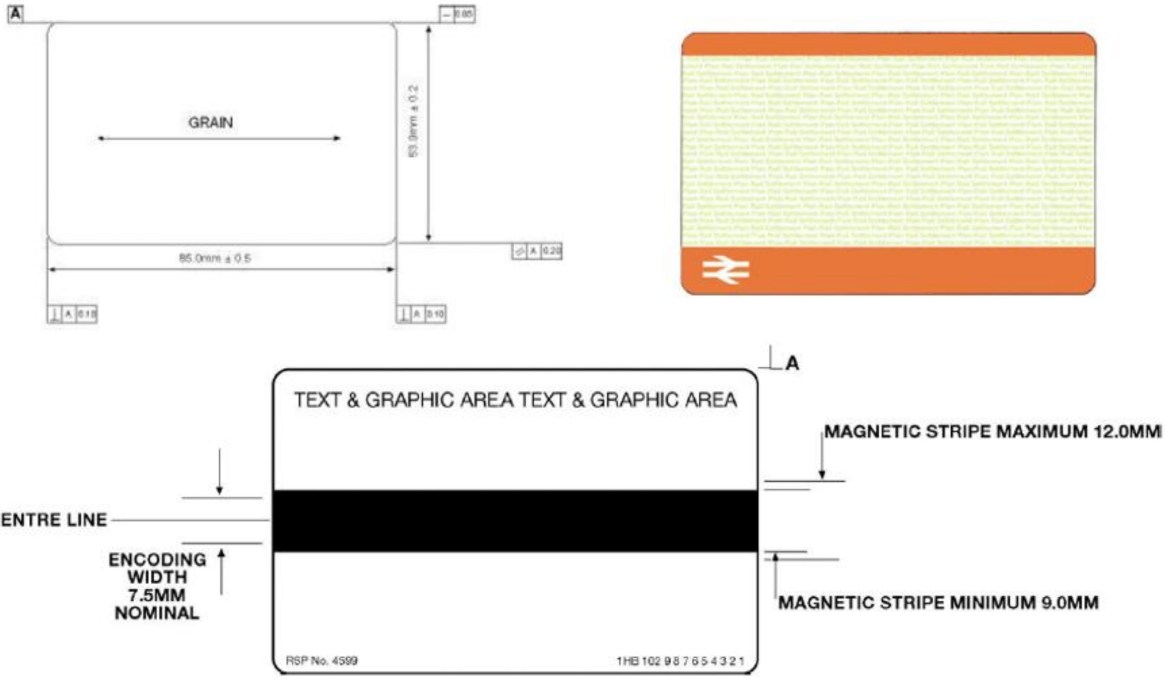
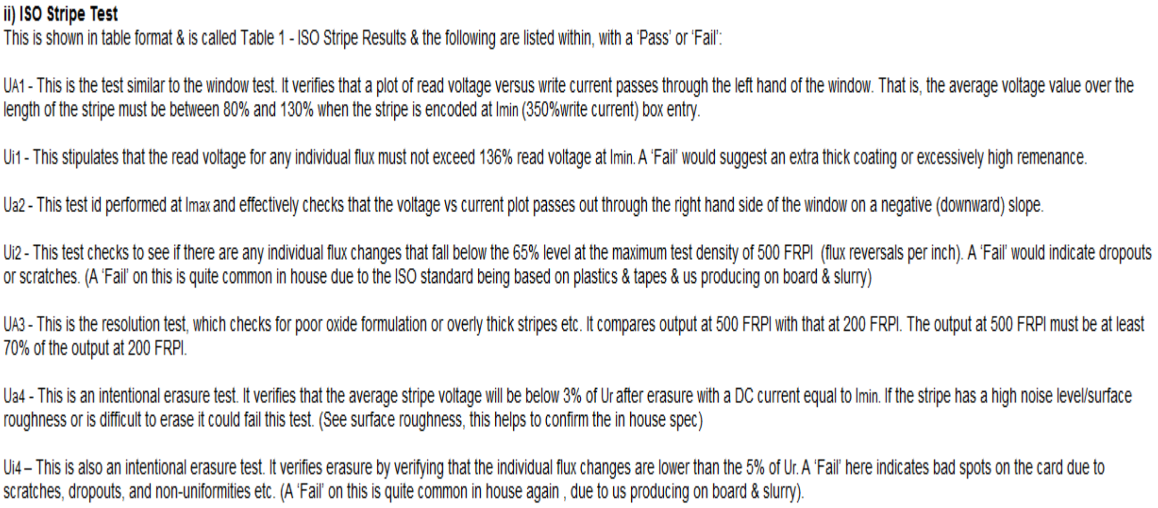


Figure 2.32: Schematic of final product once Flexographic printing process is complete.

The following figures (2.33 and 2.34) explain the readings taken (from the ISO Standard for magnetic tickets) during and post manufacture, and why each parameter is important.



ii) ISO Stripe Test
This is shown in table format & is called Table 1 - ISO Stripe Results & the following are listed within, with a 'Pass' or 'Fail':

UA1 - This is the test similar to the window test. It verifies that a plot of read voltage versus write current passes through the left hand of the window. That is, the average voltage value over the length of the stripe must be between 80% and 130% when the stripe is encoded at Imin (350%write current) box entry.

Ui1 - This stipulates that the read voltage for any individual flux must not exceed 136% read voltage at Imin. A 'Fail' would suggest an extra thick coating or excessively high remenance.

Ua2 - This test id performed at Imax and effectively checks that the voltage vs current plot passes out through the right hand side of the window on a negative (downward) slope.

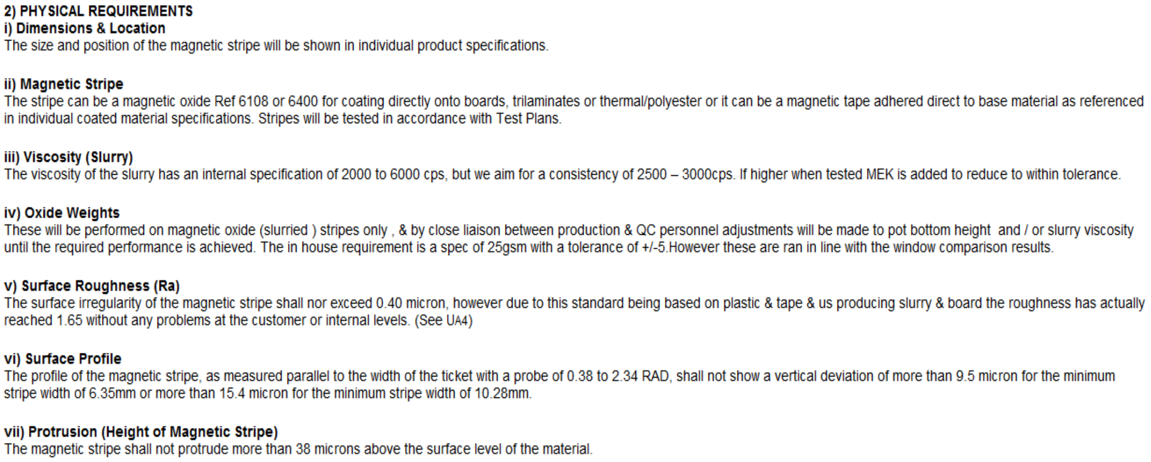
Ui2 - This test checks to see if there are any individual flux changes that fall below the 65% level at the maximum test density of 500 FRPI (flux reversals per inch). A 'Fail' would indicate dropouts or scratches. (A 'Fail' on this is quite common in house due to the ISO standard being based on plastics & tapes & us producing on board & slurry)

UA3 - This is the resolution test, which checks for poor oxide formulation or overly thick stripes etc. It compares output at 500 FRPI with that at 200 FRPI. The output at 500 FRPI must be at least 70% of the output at 200 FRPI.

Ua4 - This is an intentional erasure test. It verifies that the average stripe voltage will be below 3% of Ur after erasure with a DC current equal to Imin. If the stripe has a high noise level/surface roughness or is difficult to erase it could fail this test. (See surface roughness, this helps to confirm the in house spec)

Ui4 – This is also an intentional erasure test. It verifies erasure by verifying that the individual flux changes are lower than the 5% of Ur. A 'Fail' here indicates bad spots on the card due to scratches, dropouts, and non-uniformities etc. (A 'Fail' on this is quite common in house again , due to us producing on board & slurry).

Figure 2.33: Magnetic ISO 7811-2/6 Test Descriptions



2) PHYSICAL REQUIREMENTS
i) Dimensions & Location
The size and position of the magnetic stripe will be shown in individual product specifications.

ii) Magnetic Stripe
The stripe can be a magnetic oxide Ref 6108 or 6400 for coating directly onto boards, trilaminates or thermal/polyester or it can be a magnetic tape adhered direct to base material as referenced in individual coated material specifications. Stripes will be tested in accordance with Test Plans.

iii) Viscosity (Slurry)
The viscosity of the slurry has an internal specification of 2000 to 6000 cps, but we aim for a consistency of 2500 – 3000cps. If higher when tested MEK is added to reduce to within tolerance.

iv) Oxide Weights
These will be performed on magnetic oxide (slurried) stripes only , & by close liaison between production & QC personnel adjustments will be made to pot bottom height and / or slurry viscosity until the required performance is achieved. The in house requirement is a spec of 25gsm with a tolerance of +/-5.However these are ran in line with the window comparison results.

v) Surface Roughness (Ra)
The surface irregularity of the magnetic stripe shall nor exceed 0.40 micron, however due to this standard being based on plastic & tape & us producing slurry & board the roughness has actually reached 1.65 without any problems at the customer or internal levels. (See UA4)

vi) Surface Profile
The profile of the magnetic stripe, as measured parallel to the width of the ticket with a probe of 0.38 to 2.34 RAD, shall not show a vertical deviation of more than 9.5 micron for the minimum stripe width of 6.35mm or more than 15.4 micron for the minimum stripe width of 10.28mm.

vii) Protrusion (Height of Magnetic Stripe)
The magnetic stripe shall not protrude more than 38 microns above the surface level of the material.

Figure 2.34: Physical specification for UK Rail products.

The magnetic ink produced for PID in Argent is coated *via* rotogravure; in the factory at Argent, there are two rotogravure slurry coaters. These machines transfer slurry from a received slurry tin to a flexible substrate, for example PVC, PET or paper board. There are two additional processes; one is to cut the coated reel into smaller reels and the second is to print in colour on the *verso* of the coated substrate. The end product has to conform to a customer specification and this determines whether the reel is magnetically encoded or not, the type of complex printing on the *verso* side and the packaging required for the final product.

The slurry is pumped using air to the coating cylinder to ensure the transfer of slurry to the board. Chrome-plated steel cylinders (*cylinders d'enducation*), with grooves that are typically between 130-380 µm deep, are employed for the motorway slurry. In other cases rubber or ceramic cylinders can be used depending on the roughness and the hardness required for the end application. It is noteworthy that these cylinders differ not only in width and depth of the cell, but also the pattern that is engraved at the bottom – this can be hexagonal or octagonal. As with the Hull process, the substrate with the wet magnetic ink passes through a magnet and is sent through an oven to dry. This substrate however is not thermally based and so can be dried at higher temperatures – the process flow is represented in figure 2.35 below.

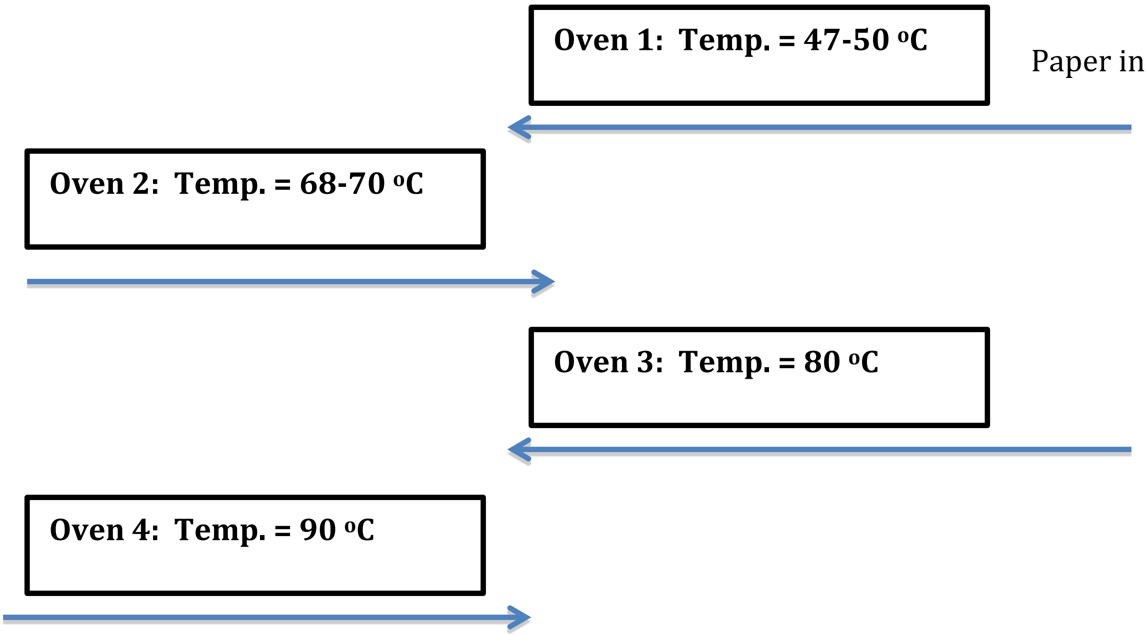


Figure 2.35: Rotogravure oven layout in Argent.

Once coated reels have been produced, they are subjected to a flexography conversion process whereby the blank tickets with the dried magnetic stripes are converted through flexography printing with normally coloured inks.

2.6 Printing Methods

A large number of printing techniques have been developed over the previous 1000 years. Current commercial methods include lithographic, flexographic, offset, gravity, gravure, screen, 3D and digital. Flexographic printing is used daily at BemroseBooth Paragon.

The flexography printing technique incorporates a flexible relief plate made from photopolymer. 'Flexo' is advantageous as it can be utilized to print on almost any type of substrate including plastic, metallic films, cellophane, and paper. The magnetic ink coated rolls produced in BBP Hull are converted into final products *via* flexography.

2.6.1 Operational overview

Figure 2.36 shows these components in action.

1) Fountain roller

The fountain roller transfers the ink to the second roller from the ink pan. This is called the anilox or 'metering' roller

2) Anilox roller

The anilox roller meters the ink being transferred to ensure uniform thickness. It has microscopically sized engraved cells that carry a specified capacity of ink. This roller transfers the ink to the flexible-plates that are mounted on the Plate Cylinders.

3) Doctor Blade (optional)

The doctor blade scrapes the anilox roller to ensure that excess ink is removed only what is contained within the engraved cells is delivered. Doctor blades have predominantly been made of steel but advanced doctor blades are now made of polymer materials.

4) Plate cylinder

The plate cylinder holds the photopolymer printing plate, which is soft flexible rubber-like material. The printing plate is held against the cylinder with double sided adhesive.

5) Impression Cylinder

The impression cylinder applies pressure to the plate cylinder, allowing the image to be transferred to the substrate.

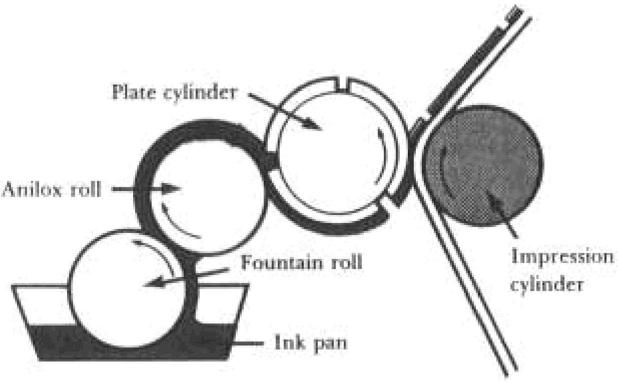


Figure 2.36: Flexographic image carriers [11].

2.6.2 Advantages of Flexography

- Runs at extremely high press speeds (150 m/min at BBP Hull).
- Prints on a wide variety of substrate materials.
- Low cost of equipment and maintenance.
- Relatively low cost of most consumables.
- Ideally suited for long runs.
- All printing, varnishing, laminating and die cutting done in a single pass.

2.6.3 Disadvantages of Flexography

- The cost of the flexo printing plates is relatively high, but when they are properly cared for, they last for millions of impressions.
- It takes several hours to set up complex jobs that print, varnish, laminate and die cut.
- Takes a large amount of substrate to set up the job, potentially wasting expensive material.
- If version changes are necessary, they are time-consuming to make.

Within the dried stripe in the final product (figure 2.37) are particles of iron oxide, a form of common red rust. Gamma ferric oxide (γ-Fe_2O_3) and Fe_3O_4 are oxides of iron commonly known as maghemite and magnetite respectively [2]. This oxide is a ferrimagnetic material, meaning that when exposed to a magnetic field it becomes permanently magnetized.

Figure 2.37: Rail Ticket with Magnetic Ink Stripe manufactured at BBP [12].

The blank stripe is encoded or “written” by the “write head” within the rail ticket dispensing equipment, which creates a series of magnetic strips that lie perpendicular to the length of the stripe. The particles are positioned pointing either towards the North or South Poles and the strips are produced with varying degrees of thickness, thus creating a type of binary magnetic barcode. See figure 2.38. This unique series of magnetic strips holds information such as location of purchase, ticket purchase price, destination, date and time etc.

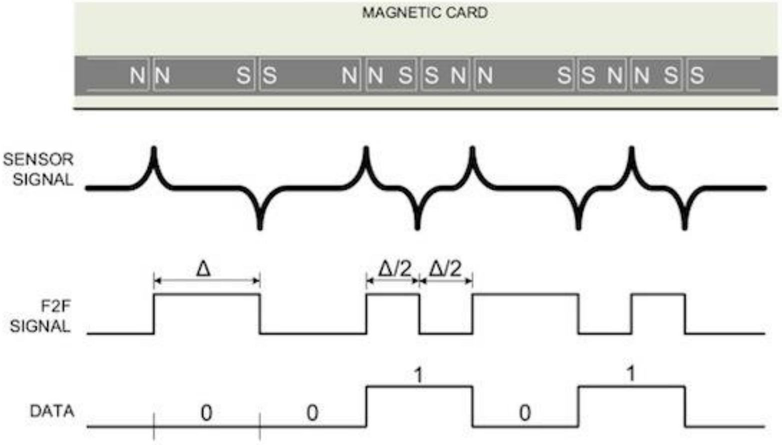


Figure 2.38: Binary information stored on a magnetic stripe. [13]

In order for the ticket information to be decoded or “read” the magnetic stripe passes across a “read head” which decodes the magnetic barcode by sensing the direction of magnetism of the individual strips and their varying thicknesses. This information is then sent electronically to the ticketing companies’ central computer database which recognises the ticket information, and verifies a match of information with the particular ticket within seconds, allowing the user to pass through a gate or barrier.

The intrinsic magnetic properties of the product also hold an explanation for the performance of the ticket. Whilst utilising the magnetic ink products for each of their applications, an external magnetic field of strength H is applied to "read" the information stored in the magnetic material. When this happens the magnetisation of the material M strengthens along with H until a saturation value M_S [14]. When H decreases, M does not follow the pattern creating a hysteresis loop on the magnetisation curve and leaving a remnant magnetisation M_R when H returns to zero. To remove M_R, a coercive field Hc has to be applied in the opposite direction to the initial field H. The magnetisation curve is displayed in Figure 2.39.

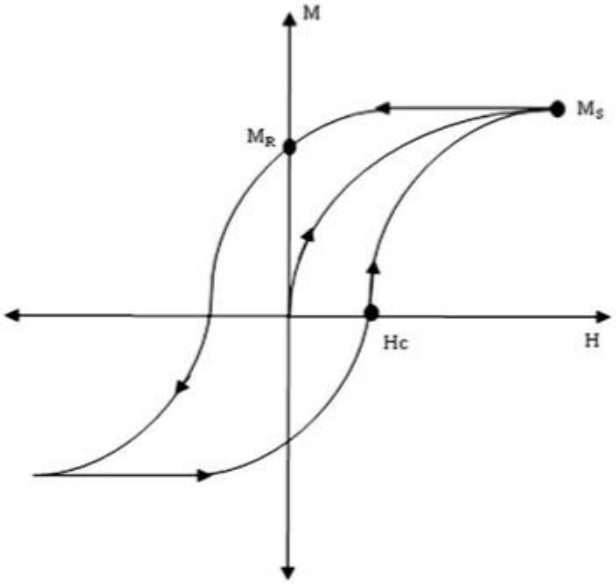


Figure 2.39: Hysteresis Cycle [14].

In the case of magnetic inks being employed in the ticketing industry, an optimum ink should exhibit a high coercivity as possible within the specification (so it will not be easily demagnetized and “lose" the information that was stored), high squareness (indicating that the ticket retains information well) and a low switching field distribution (which means that the coated ink is magnetically uniform). Also, the ticket should be resistant to corrosion, friction and temperature changes, whilst being insoluble in palm sweat, rain *etc.*

Throughout this thesis, the following definitions will be used:

Coercivity (Hc) is the point when the magnetization curve equals zero. Strictly this is the arithmetic mean of both positive and negative Hc values on the curve.

Squareness is equal to M_R/M_S; this ratio depends strongly on the value of the maximum applied field. The accuracy of squareness measurements is dependent on the ability to set the maximum applied field to a reproducible value.

SF_D is the width at half-maximum of the first derivative of the re-magnetization curve. The measurement of SF_D is particularly vulnerable to errors arising from small changes on the M=f(H) curve as it uses a derivative relation.

References

[1] http://www.idc-online.com/technical_references/pdfs/electrical_engineering/What_is_Magnetism.pdf - Accessed 04/05/2017
[2] http://www.ucl.ac.uk/EarthSci/people/lidunka/GEOL2014/Geophysics9%20-Magnetism/Useful%20papers/Magnetism.htm Accessed 05/05/2017 - Accessed 04/05/2017
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[5] http://www.inkline.gr/inkjet/newtech/tech/dispersion/ - Accessed 11/07/2017
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[14] A. S. Teja, P. Koh, *Progress in Crystal Growth and Characterization of Materials*, 2009, **55**, 22-45.

Chapter 3 – Design Specification

The project involved both the transfer of existing formulations from one manufacturing site to another, and the development of further formulations in the new facility to add products to the manufacturing line one qualified with the customer.

In total, thirteen magnetic ink formulations were requested, each of which varied in end user performance requirements. Determining the technical specification of the products was key in deducing the design of the manufacturing process, process engineering and formulation chemistry.

Table 3.1 below identifies each project product and a description:

Table 3.1: Magnetic Inks Formulated.

Product Code	Description/Application
HL0104 (LoCo)	Motorway toll tickets in France.
FHL0201 (LoCo)	Paris, Cairo and Caracas Metro tickets
HL0301 (LoCo)	UK Rail Ticket for RDG
HL0401 (LoCo)	Brazilian Metro tickets and bank notes
HL0501 (LoCo)	RAM Systems cards
HL0601 (LoCo)	Low-output tickets for energy tokens
HH0104 (HiCo)	Various PID customers
HH0201 (HiCo)	Various PID customers
HH0307 (HiCo)	Various PID customers
HH0401 (HiCo)	Nexus Rail ticket
HH0501 (HiCo)	Hegard Poland bus tickets
HH0601 (HiCo)	Various PID customers
HH0702 (HiCo)	New York Metro tickets

Of the products described in Table 2, two were pre-customer approved before the transfer of manufacturing (HL0301 and HH0401) as they were already used in production at BBP. The remaining formulations required some development work and manipulation in manufacturing to achieve the desired results.

The design specification for these magnetic ink products were identified and are represented in the following section.

HL0104:

Appearance

- Colour: Black/dark brown.
- Quantity: 20 kg net drum
- Solids content when delivered: 43.0 ± 3.0
- Solvent: Isopropyl Acetate.
- Type of binder: Vinyl copolymer.

Principal application/uses

- Thin coatings onto various substrates.
- With rotogravure process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

- Coercivity (Oe): 315 ± 25
- Squareness: ≥ 0.70
- SFD: ≤ 0.70

Physical and rheological characteristics

- Specific gravity : 1.24 (kg/L) as wet slurry at a solid content of 43%
- Brookfield viscosity (Centipoise): 1600 ± 500

Mechanical characteristics

- Specific gravity: 2.71 (kg/L) as dry coating.
- Electrical Square resistance (ohms): 10^{10}

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content : 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 mins : spindle n° 5 LVS, speed 100 rpm, Factor 40

- Magnetism (temperature 23°C ± 2°C);

BH Looper at 1500 Oe on orientated coating with standard magnet.

FHL0201:

Appearance

• Colour:	Brown.
• Quantity:	20 kg net drum.
• Solids content when delivered:	43.0 ± 3.0
• Solvent:	Isopropyl Acetate.
• Type of binder:	vinyl copolymer.

Principal application/uses

- Thin coatings onto various substrates.
- With rotogravure process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics

• Coercivity (Oe):	335 ± 12
• Squareness:	≥ 0.70
• SFD:	≤ 0.70

Physical and rheological characteristics

• Specific gravity:	1.24 (kg/L) as wet slurry at a solid content of 44%
• Brookfield viscosity (Centipoise):	1600 ± 500

Mechanical characteristics

• Specific gravity:	2.71 (kg/L) as dry coating.
• Electrical Square resistance (ohms):	10^{10}

Procedures

- Measurements at 23 °C (± 2°C)
- Solid content : 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 min : spindle n° 5 LVS, speed 100 rpm, Factor 40

- Magnetism (temperature 25°C ± 2°C);

BH Looper at 1500 Oe on orientated coating with standard magnet.

HL0301:

Appearance

• Colour:	Black/dark brown.
• Quantity:	180 kg net drum
• Solids content when delivered:	40.0 ± 3.0
• Solvent/Carrier:	Methyl Ethyl Ketone, Tetrahydrofuran.
• Type of binder:	Rubber based.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

• Coercivity (Oe):	320 ± 50
• Squareness:	≥ 0,70
• Switching Field Distribution:	≤ 0,70

Physical and rheological characteristics

• Specific gravity:	1.24 (kg/L) as wet slurry at a solid content of 43%.
• Brookfield viscosity (Centipoise):	4000 ± 1000

Mechanical characteristics

• Specific gravity:	2.71 (kg/L) as dry coating.
• Electrical Square resistance (ohms):	10^{10}

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content: 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity; Spin for a minimum of 2 min : spindle n° 5 LVS, speed 20 rpm, Factor 200
- Magnetism (temperature 23°C ± 2°C), LoCo: BH Looper at 1500 Oe on orientated coating with standard magnet.

HL0401:

Appearance

- Colour: Brown.
- Quantity: 20kg net drum.
- Solids content when delivered: 45.0 ± 2.0
- Solvent: Methyl Ethyl Ketone, Isopropyl Acetate.
- Type of binder: Vinyl copolymer.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

- Coercivity (Oe): 320 ± 50
- Squareness: ≥ 0,70
- SFD: ≤ 0,70

Physical and rheological characteristics

- Specific gravity : 1.24 (kg/L) as wet slurry at a solid content of 43%
- Brookfield viscosity (Centipoise): 50 to 80 TV. Not known in centipoise.

Mechanical characteristics

- Specific gravity : 2.71 (kg/L) as dry coating.
- Electrical Square resistance (ohms) : 10^{10}

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content: 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 min : spindle n° 5 LVS, speed 100 rpm, Factor 40

- Magnetism (temperature 23°C ± 2°C)

BH Looper at 1500 Oe on orientated coating with standard magnet.

HL0501:

Appearance

• Colour:	Brown.
• Quantity:	20 kg net drum.
• Solids content when delivered:	40.0 ± 2.0
• Solvent:	Methyl Ethyl Ketone.
• Type of binder:	Vinyl Copolymer.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

• Coercivity (Oe):	320 ± 50
• Squareness:	≥ 0.70
• SFD:	≤ 0.70

Physical and rheological characteristics

• Specific gravity:	1.24 (kg/L) as wet slurry at a solid content of 43%
• Brookfield viscosity (Centipoise):	4000 ± 1000

Mechanical characteristics

• Specific gravity :	2.71 (kg/L) as dry coating.
• Electrical Square resistance (ohms) :	10^{10}

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content : 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 min : spindle n° 5 LVS, speed 20 rpm, Factor 200

- Magnetism (temperature 23°C ± 2°C)

BH Looper at 1500 Oe on orientated coating with standard magnet.

HL0601:

Appearance

- Colour: Brown.
- Quantity: 20 kg net drum.
- Solids content when delivered: 44.0 ± 2.0
- Solvent: Methyl Ethyl Ketone.
- Type of binder: Vinyl copolymer.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

- Coercivity (Oe): 315 ± 25
- Squareness: ≥ 0.70
- SFD: ≤ 0.70

Physical and rheological characteristics

- Specific gravity: 1.24 (kg/L) as wet slurry at a solid content of 43%
- Brookfield viscosity (Centipoise): 2050 ± 250

Mechanical characteristics

- Specific gravity: 2.71 (kg/L) as dry coating.
- Electrical Square resistance (ohms): 10^{10}

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content : 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 mins : spindle n° 4 LVS, speed 50 rpm, Factor ?

- Magnetism (temperature 23°C ± 2°C)

BH Looper at 1500 Oe on orientated coating with standard magnet.

<u>HH0104:</u>

Appearance

• Colour:	Black/dark red.
• Quantity:	20 kg net drum.
• Solids content when delivered:	52.5 ± 2.5%
• Solvent:	Methyl Ethyl Ketone.
• Type of binder:	Rubber based.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

• Coercivity (Oe):	2700 ± 270
• Squareness:	≥ 0.80
• SFD:	≤ 0.70

Physical and rheological characteristics

• Specific gravity:	1.29 (kg/L) as a wet slurry
• Brookfield viscosity (Centipoise):	2100 ± 200

Mechanical characteristics

• Specific gravity:	3 (kg/L) as dry coating.
• Electrical Square resistance (ohms):	10^8

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content : 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 min : spindle n° 4 LVS, speed 50 rpm, Factor 40

- Magnetism (temperature 23°C ± 2°C)

BH Looper at 15000 Oe on orientated coating with special magnet.

HH0201:

Appearance

- Colour: Black/dark red.
- Quantity: 20 kg net drum.
- Solids content when delivered: 52.5 ± 2.5%
- Solvent: Methyl Ethyl Ketone.
- Type of binder: Rubber based.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

- Coercivity (Oe): 2700 ± 270
- Squareness: ≥ 0.80
- SFD: ≤ 0.70

Physical and rheological characteristics

- Specific gravity: 1.29 (kg/L) as a wet slurry
- Brookfield viscosity (Centipoise): 2100 ± 200

Mechanical characteristics

- Specific gravity: 3 (kg/L) as dry coating.
- Electrical Square resistance (ohms): 10^8

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content: 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 min : spindle n° 4 LVS, speed 50 rpm, Factor 40

- Magnetism (temperature 23°C ± 2°C)

BH Looper at 15000 Oe on orientated coating with special magnet.

Note: Electrical level readings must not be as normal ISO standard for coating, level must be reduced to 45-65%.

HH0307:

Appearance

- Colour: Black/dark red.
- Quantity: 20 kg net drum.
- Solids content when delivered: 52.5 ± 2.5%
- Solvent: Methyl Ethyl Ketone.
- Type of binder: Rubber based.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

- Coercivity (Oe): 3500 ± 270
- Squareness: ≥ 0.80
- SFD: ≤ 0.70

Physical and rheological characteristics

- Specific gravity: 1.29 (kg/L) as a wet slurry
- Brookfield viscosity (Centipoise): 2100 ± 200

Mechanical characteristics

- Specific gravity: 3 (kg/L) as dry coating.
- Electrical Square resistance (ohms): 10^8

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content: 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 min : spindle n° 4 LVS, speed 50 rpm, Factor 40

- Magnetism (temperature 23°C ± 2°C)

BH Looper at 15000 Oe on orientated coating with special magnet.

HH0401:

Appearance

- Colour: Black/dark red.
- Quantity: 20 kg net drum.
- Solids content when delivered: 51.0 ± 2.0%
- Solvent: Methyl Ethyl Ketone , Tetrahydrofuran.
- Type of binder: Rubber based.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

- Coercivity (Oe): 2700 ± 500
- Squareness: ≥ 0.70
- SFD: ≤ 0.70

Physical and rheological characteristics

- Specific gravity: 1.29 (kg/L) as a wet slurry
- Brookfield viscosity (Centipoise): 4000 ± 1000

Mechanical characteristics

- Specific gravity: 3 (kg/L) as dry coating.
- Electrical Square resistance (ohms): 10^8

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content : 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 min : spindle n° 5 LVS, speed 20 rpm, Factor 200

- Magnetism (temperature 23°C ± 2°C)

BH Looper at 15000 Oe on orientated coating with special magnet.

HH0501:

Appearance

• Colour:	Black/dark red.
• Quantity:	20 kg net drum.
• Solids content when delivered:	51.0 ± 2.0%
• Solvent:	Methyl Ethyl Ketone , Tetrahydrofuran.
• Type of binder:	Rubber based.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

• Coercivity (Oe):	3500 ± 500
• Squareness:	≥ 0.70
• SFD:	≤ 0.70

Physical and rheological characteristics

• Specific gravity:	1.29 (kg/L) as a wet slurry
• Brookfield viscosity (Centipoise):	4000 ± 1000

Mechanical characteristics

• Specific gravity:	3 (kg/L) as dry coating.
• Electrical Square resistance (ohms):	10^8

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content : 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 min : spindle n° 5 LVS, speed 20 rpm, Factor 200

- Magnetism (temperature 23°C ± 2°C)

BH Looper at 15000 Oe on orientated coating with special magnet.

HH0601:

Appearance

- Colour: Black/dark red.
- Quantity: 20 kg net drum.
- Solids content when delivered: 52.5 ± 2.5%
- Solvent: Methyl Ethyl Ketone.
- Type of binder: Rubber based.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

- Coercivity (Oe): 3500 ± 270
- Squareness: ≥ 0.80
- SFD: ≤ 0.70

Physical and rheological characteristics

- Specific gravity: 1.29 (kg/L) as a wet slurry
- Brookfield viscosity (Centipoise): 2100 ± 200

Mechanical characteristics

- Specific gravity: 3 (kg/L) as dry coating.
- Electrical Square resistance (ohms): 10^8

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content: 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 min : spindle n° 4 LVS, speed 50 rpm, Factor 40

- Magnetism (temperature 23°C ± 2°C)

BH Looper at 15000 Oe on orientated coating with special magnet.

Note: Electrical level readings must not be as normal ISO standard for coating, level must be reduced to 45-65%.

HH0702:

Appearance

- Colour: Black/dark red.
- Quantity: 180 kg net drum.
- Solids content when delivered: 52.5 ± 2.5%
- Solvent: Methyl Ethyl Ketone.
- Type of binder: Rubber based.

Principal application/uses

- Thin coatings onto various substrates.
- With gravity fed process.
- Paper, PVC, treated PET and polyester.

Magnetic characteristics (coated product)

- Coercivity (Oe): 2700 ± 300
- Squareness: ≥ 0,80
- SFD: ≤ 0,70

Physical and rheological characteristics

- Specific gravity: 1.29 (kg/L) as a wet slurry
- Brookfield viscosity (Centipoise): 4000 ± 1000

Mechanical characteristics

- Specific gravity: 3 (kg/L) as dry coating.
- Electrical Square resistance (ohms): 10^8

Procedures

- Measurements at ambient temperature (23 °C ± 2°C)
- Solid content : 30 mins at 105-110 °C, with ventilation.
- Brookfield viscosity;

Spin for a minimum of 2 min : spindle n° 4 LVS, speed 50 rpm, Factor 40

- Magnetism (temperature 23°C ± 2°C)

BH Looper at 15000 Oe on orientated coating with special magnet.

The original budget for the project was set at £150,000 to produce four magnetic ink products, however, due to a snowball effect in accruing orders and customers, it rapidly became evident that the level of spend was hugely underestimated. In order to comply fully to the ATEX regulations and integrate enough machines to meet customer demand, an increased budget of 100-150% was deemed necessary.

The next chapter details the characterization methods of the produced ink formulations.

Chapter 4 – Characterization of Magnetic Inks

The primary reason for this project was to remove an at-risk area of the supply chain for BBP. The two remaining magnetic ink suppliers in Europe were both unstable; the Director of Ferron Magnetic Inks, Ltd, UK was due to retire imminently, with no plans to continue operations, and Pyral, based in France were entering administration. Although unknown at the start of the project, a third magnetic ink manufacturer/coater (Magnadata), a direct competitor to BBP was heading for financial instability. The company would later be acquired with ink manufacturing capability to be integrated in Hull.

Before embarking upon the construction of a full-scale manufacturing facility, inks obtained from the current suppliers were characterised at a lab scale to evaluate the possibility of reverse engineering the products, and to ensure plant design would meet the requirements to produce an in-specification magnetic ink on a consistent basis.

4.1 Characterization Methods

Characterisation was executed on the products in their various stages of manufacture to obtain optimum understanding and enable the design of the production process. Wet magnetic inks were analysed, as were the solid magnetic pigment particles used in their formulation, and the final printed commercial product.

4.1.1 Wet Ink Characterisation Techniques

The wet ink characterisation was undertaken through several routes, categorised mainly under physicochemical and magnetic performance, the methods for which are explained below.

UV-Visible Spectrometry

In this experiment the absorption of monochromatic light by a solution is described by the Beer-Lambert law. A light passes through a monochromator that selects one wavelength of intensity. This passes through a sample with a selected path length and another intensity of light emerges from the other side of the sample.

The first spectrum was taken with the 'blank' solvent solution (depending on the solvent that the ink is diluted with - isopropyl acetate, methyl ethyl ketone or tetrahydrofuran). A solution of the inks were then prepared, at a concentration of 0.1% in solvent. HL0301 and HH0401 were diluted in MEK, FHL0201 in IPAC and the others in THF. The inks were then analysed.

pH

pH is a measure of the acidity or basicity of an aqueous solution. It can be expressed as the negative logarithm of the hydronium ion activity in the solution. The pH of the inks were measured by placing them inside of a glass tube and the pH probe was lowered into the ink. The measured pH and temperature of the ink were then recorded. Although this is a poor method for determination of pH in an organic solvent, it is the only method currently available.

Solid (Mass) Content

Solid or mass content is the proportion of non-volatile material left after the volatile solvent has vaporized. The following procedure was adopted to obtain solid content. The mass of a glass container was measured, then 1 mL of the ink was pipetted onto the glass and weighed again. After this, the sample was heated in an oven for 30 minutes at the temperature of 90 °C. After drying, the weight of the sample was measured again before placing back inside the oven for another 30 minutes. The weight of the 'dried' inks remained constant at both points of measurement so there was no need for the secondary 30 minutes in the following tests.

To calculate the solid content of the sample the following equation was applied.

$$\% \text{ Solid Content} = 100 \times \frac{(\text{Dried Mass in Tray/g})}{(\text{Wet Mass in Tray/g})} \qquad \text{Eq 4.1}$$

Water content - Karl Fischer

Karl Fischer titration is a classic titration method in analytical chemistry that uses coulometric or volumetric titration to determine trace amounts of water in a sample, in this experiment the coulometric titration was adopted. The conventional method works with a methanolic solution of iodine, sulfur dioxide and a buffer substance. The following equation summarizes the reaction:

$$H_2O + I_2 + [RNH]SO_3CH_3 + 2RN \rightleftarrows [RNH]SO_4CH_3 + 2[RNH]I \qquad \text{Eq 4.2}$$

According to this equation, the water and I_2 are in the same proportion, so they react quantitatively. In the titration, the necessary iodine is directly and electrochemically generated in the electrolyte. There is a relationship between the amount of electric charge and the amount of generated iodine which is used for the high-precision dosing of iodine.

To measure the water content in the HL0104 and FHL0201 samples, the inks were diluted in IPAC to prepare solutions of concentration 1% and 10%. After this, 1 mL of pure IPAC was put in the 899 coulometer using the Karl Fischer method. The ink solutions were then subjected to the same procedure to obtain the water content.

4.1.2 Solid Pigment Characterization Techniques

The functional raw material used in magnetic ink formulation was characterized to understand the qualities required from the magnetic pigments to create the desired final product. The techniques are detailed as follows.

X-Ray Diffraction

X-Ray diffraction was performed to determine pigment purity crystallinity. In XRD analysis, the sample is subjected to a focused X-Ray beam at a specific angle of incidence. The X-Rays diffract differently depending on the crystal structure of the sample. The angles and intensities of the deflected X-Rays are measured.

Scanning Electron Microscope (SEM/EDX)

The pigments were subjected to SEM analysis to understand surface topography and elemental composition.

Magnetic Characterization

The test specimen is to be removed directly from the source (pigment bag) prior to use for manufacture. A controlled level of pigment is mixed with dual component Loctite before being placed in a mould to create a cuboidal shaped sample. The sample is mounted onto a polyester stick and loaded into the BH Looper to test magnetically.

4.1.3 Final Printed Product Characterization Techniques

Commercially available final products were also tested to understand final product characteristics.

Surface properties

Two instruments were employed to understand the surface profiling of the magnetic stripe in its final form on ticket products. This information influences the properties of the formulation, particularly with respect to the substrate that the ink is printed on.

Magnetic Characterization

In magnetic characterizations, the slurry needs to be proofed as a thin film and then inserted in the BH Looper sensor head, formed by a toroidal ring. As current passes through the loops, a magnetic field (determined by the number of loops of the current) arises allowing the corresponding flux density to be measured. After the measurement, a hysteresis curve is produced and key parameters obtained.

The key parameters are coercivity, squareness and SFD. The coercivity relates to the resistance of a magnetic material to changes in magnetization, squareness is associated with the rectangularity of the hysteresis and SFD is related to the dispersion of coercivity within the particles.

4.2 Characterization of Supplied Inks

4.2.1 Wet Magnetic Ink Characterization

The inks characterized are stated in Table 4.1.

Table 4.1: Inks Characterized.

Product Code	Coercivity Type	Supplier
HL0301	Low	Ferron
HL0104	Low	Pyral
FHL0201	Low	Pyral
HH0401	High	Ferron
HH0401	High	Pyral
HH0307	High	Pyral

Techniques Used

Analysis was completed on appearance using the UV-Vis absorption measurements, density, water content through Karl Fischer method, pH acid and moisture content (solid content).

Experimental Results

Table 4.2 shows a summary of the results for wet pigment characterizations. The full results are available in Appendix 1.

Table 4.2: Wet pigment characterizations.

Hc Type	**Product Code**	**pH Mean**	**Solid Content (%)**	**UV-Vis λ_{max} Range (nm)**	**KF H_2O Range (ppm)**	**Product Matches Spec?**
Low	HL0301	4.22	42.5	320-340	26552-26812	Yes
Low	FHL0201	6.62	31.68	700-750	2237-2262	Almost (SC out)
Low	HL0104	4.08	36.66	275-285	970-1752	Almost (SC out)
High	HH0401	7.09	24.38	n/a	402-483	No (SC out)
High	HH0307	3.30	41.83	270-280	1928-13742	Yes

4.2.2 Solid Pigment Characterization Experimental Results

Following the physicochemical characterization of the wet ink, it was important to next develop an understanding of the supply chain, particularly in reference to the magnetic pigment. There was a key focus for one particular ink, FHL0201, as the final coercivity specification requested by the customer is lower in range than that specified by the pigment supplier. This meant that the pigment needed to be tested prior to use in manufacture to ensure it was suitable for use in the final product. These analyses are also important in determining pigment properties, for example the pigments and additives need to allow for conductivity, which can be provided by carbon black, however if the oil absorption of the pigment was too high as observed with a particular grade of carbon, then high gelling properties in the final formulation are observed. This can be damaging to the coating process, for example with the formation of flocculated particles on the calendar rollers of the coating machine.

It was also important to characterize HiCo pigments also in the development of the formulations to determine the effect on the final magnetic properties determined by the ISO standards.

Techniques Used

To analyze the pigments both Scanning Electron Microscopy with EDX analysis was employed, along with XRD and magnetic characteristics using the BH Looper.

Experimental Result

Firstly, the difference in HiCo and LoCo pigments can be observed. The SEM analysis in figures 4.1 and 4.2 show the surface topography of the two pigment types at a 1 µm scale. The high coercivity particles are known as hard ferrites and are hexagonal in shape. They are typically strontium or barium containing ferrite compounds.

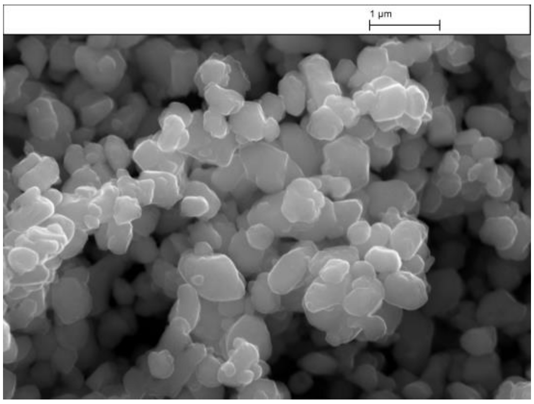


Figure 4.1: Hexagonal-shaped HiCo Pigment

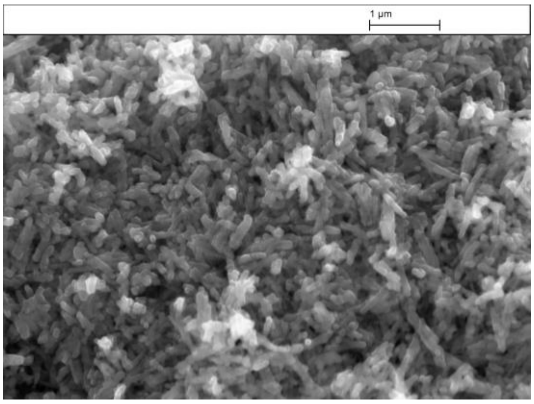
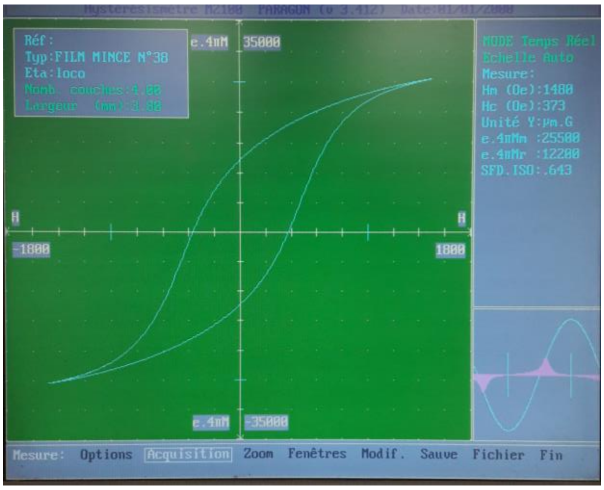


Figure 4.2: Needle shaped LoCo Pigment

These pigments were tested for magnetic characteristics as described above. As it is not possible to align the magnetic domains in a loose powder form, only the coercivity can be extracted as a useful value. For the LoCo pigment a coercivity value of 373 Oe was obtained (see figure 4.3), for the HiCo, 2800 Oe. These are both within agreeable limits of the suppliers' specification.



Hysteresismetre M2100 PARAGON (v 3.412) Date:01/01/2000

Réf:
Typ:FILM MINCE N°38
Eta:loco
Nomb. couches:4.00
Largeur (mm):3.80

MODE Temps Réel
Echelle Auto
Mesure:
Hm (Oe):1480
Hc (Oe):373
Unité Y:µm.G
e.4πMm :25500
e.4πMr :12200
SFD.ISO:.643

Figure 4.3: Low coercivity pigment test.

X-Ray diffraction was also used to determine the purity of the pigment samples. The following pigment trace is represented as gamma ferric oxide, showing some noise due to the presence of iron but no significant impurities.

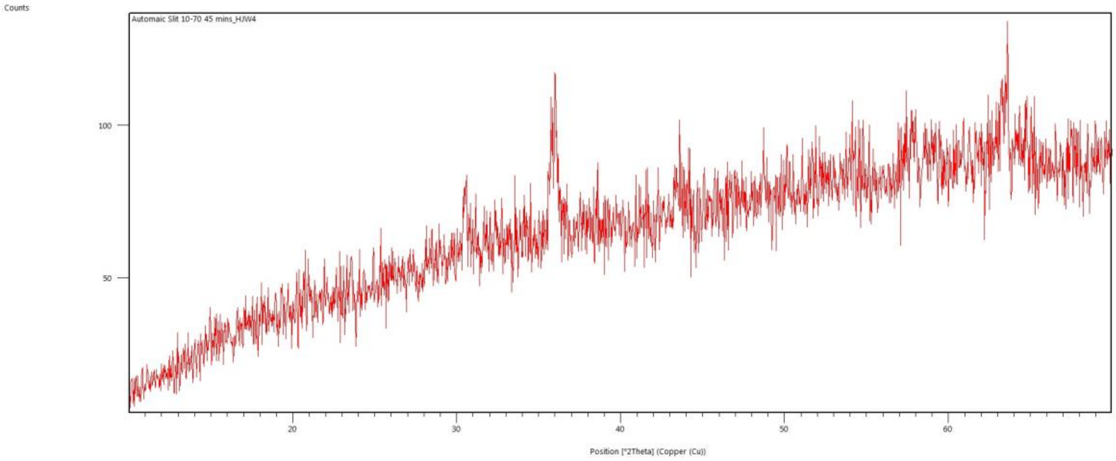


Figure 4.4: XRD trace for gamma ferric oxide.

4.2.3 Final Product Characterization Experimental Results

Techniques Used

The surface profiling of the final products were obtained through the use of two machines, the Dektak and White Light Interferometer. The BH Looper was also used to characterize the magnetic characteristics of production tickets.

Experimental Result

The Dektak and White Light Interferometer readings (figures 4.5 and 4.6 respectively) are shown below for a magnetic stripe on a polyester substrate. These images show a smooth substrate profile as they are taken on a polyester sample. A paper substrate would show a much more uneven surface. Stripe height is approximately 5-7 microns.

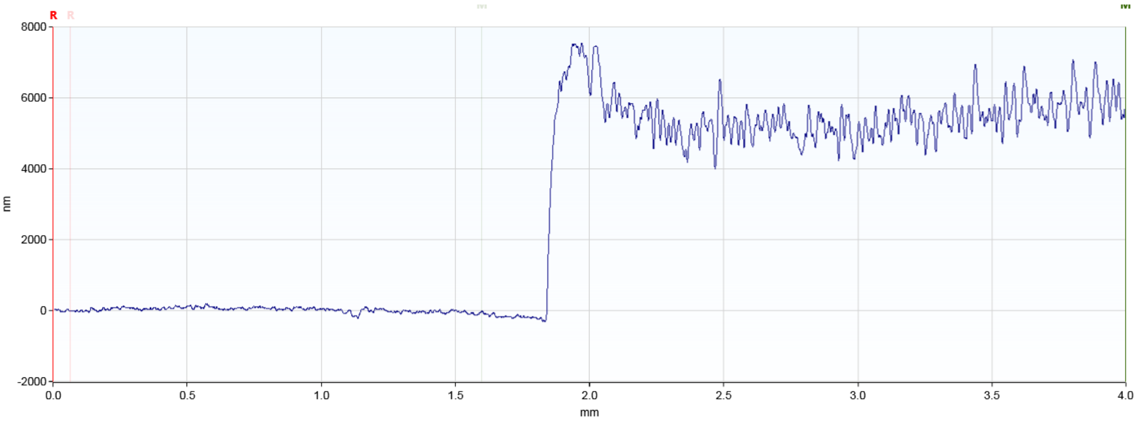


Figure 4.5: Dektak Stylus Profile (same as figure 2.20).

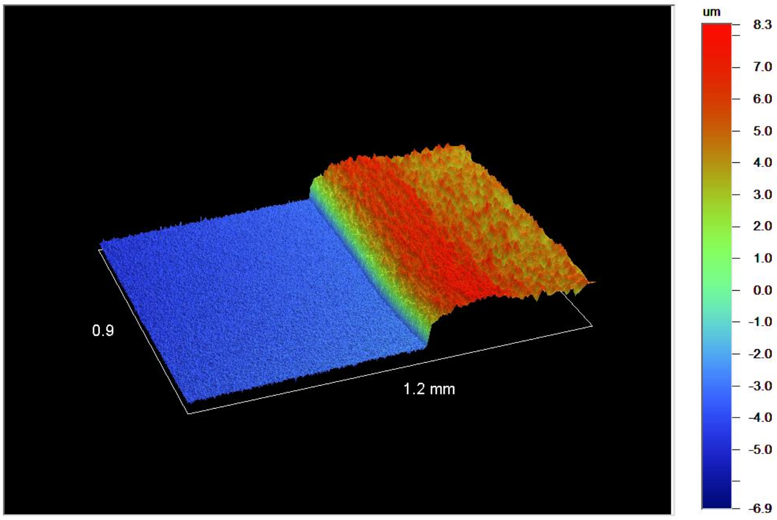


Figure 4.6: Wyko NT1100 WLI profile (same as figure 2.21).

Products HL0301, HL0104, FHL0201, HH0104 and HH0307 were tested by BH Looper to ascertain magnetic qualities versus specification so that realistic development targets could be set compared with commercially available products. Their results *vs* specification are in Tables 4.3 to 4.7, with values in red identified as out of specification.

Table 4.3: HL0301

Characteristic	**Tolerance**	**Result**
Coercivity (Oe)	320 ± 50	340
Squareness	≥ 0.70	0.782
SFD	≤ 0.70	0.656

Table 4.4: HL0104

Characteristic	**Tolerance**	**Result**
Coercivity (Oe)	315 ± 25	353
Squareness	≥ 0.70	0.737
SFD	≤ 0.70	0.606

Table 4.5: FHL0201

Characteristic	**Tolerance**	**Result**
Coercivity (Oe)	335 ± 12	351
Squareness	≥ 0.70	0.755
SFD	≤ 0.70	0.676

Table 4.6: HH0104

Characteristic	**Tolerance**	**Result**
Coercivity (Oe)	2750 ± 270	2780
Squareness	≥ 0.80	0.787
SFD	≤ 0.70	0.554

Table 4.7: HH0307

Characteristic	Tolerance	Result
Coercivity (Oe)	3500 ± 270	3670
Squareness	≥ 0.70	0.831
SFD	≤ 0.70	0.846

It is clear from the results that most formulations are within or very close to the specification on most parameters however it is notable that the products do not comply with ISO 7811/2 and 7811/6 in every case.

4.3 Characterization Conclusion

Inasmuch as the large majority of data correspond to the design specifications of the inks, it is clear that some of the inks do not conform to the expected physicochemical and magnetic properties. In the case of the wet inks, it is possible to conclude that inks HH0104 and HL0104 were damaged; most likely due to the solvent having evaporated. For the final products, the lack of magnetic conformance may be due to improper processing or an insufficiency in the raw materials used. Accordingly, these results were used as a test bed from which new formulations could be compared and areas of improvement identified.

4.4 Formulation

4.4.1 Introduction

Following initial small-scale manufacture and physicochemical characterization, it was recognized that most importantly, the magnetic characteristics must be correct for the customers approval as this is the key functional mechanism behind the final product.

Formulations were produced to create each of the slurry samples and a different milling time was applied in each case. The individual batches were characterized and tested. The parameters considered in the analysis were the following:

- Solid content;
- Magnetic characteristics:
    - Coercivity;
    - Squareness;
    - Switching Field Distribution (SFD).

The time in which the material is in the mill, together with the milling media influences the particle size [1]. Increasing milling time leads to decreasing interparticle interactions in the magnetic ink, which in turn causes an increase in coercivity and a decrease in the switching field distribution [2].

For investigation in this chapter, two formulations are considered; HL0104 and HL0301.

4.4.2 Media

The steel and ceramic balls (as shown in Figures 4.7 and 4.8) were added to the vessel containing the raw materials to accelerate the mixing process and reduce the size of the particles using shearing and impinging forces (attrition).

Figure 4.7: Ceramic Media

Figure 4.8: Steel Media

4.4.3 Equipment

For the formulation and analysis of HL0104 and HL0301, equipment used is listed and shown below.

Mini Mixer-Mill

The SPEX SamplePrep 8000M Mixer/Mill shown in Figure 4.9, also called a shaker mill or high-energy ball mill, is ideal for grinding and mixing. For the grinding process it accommodates sample sizes up to 60 mL (see vial in figure 4.10/4.11). It also has a variable-range electronic timer, set for up to a 100-minute range.

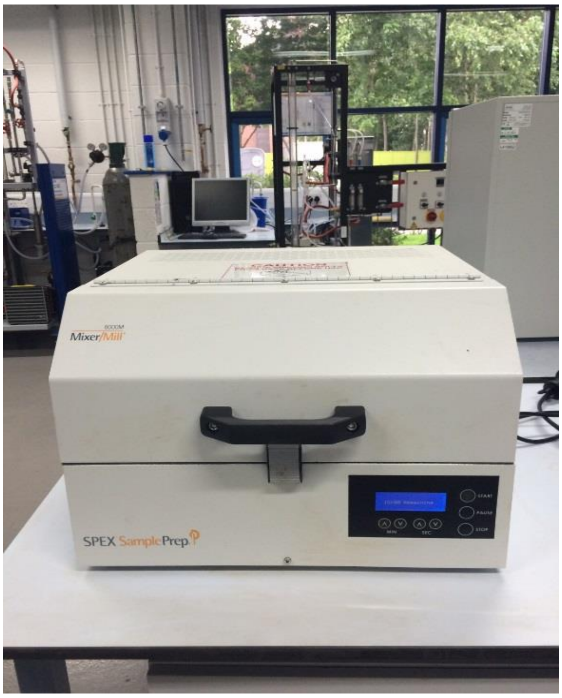


Figure 4.9: SPEX Sample Prep 8000 M Mixer Mill.

Figure 4.10: 8007 – Sample Vial for Mixer-mill.

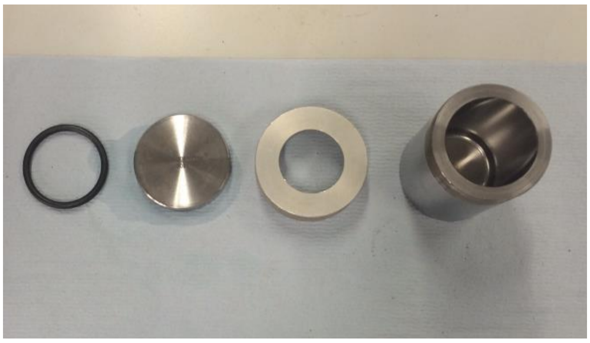


Figure 4.11: Vial, cap liner and o-ring.

Mini Attritor

Figure 4.12: Mini Attritor

Micro Attritor

Figure 4.13: Micro Attritor

Printing Proofer

The RK Print K Printing proofer with Gravure head was used to create samples coated magnetic slurries (these are orientated by bespoke magnet attachment).

Figure 4.14: K Printing proofer

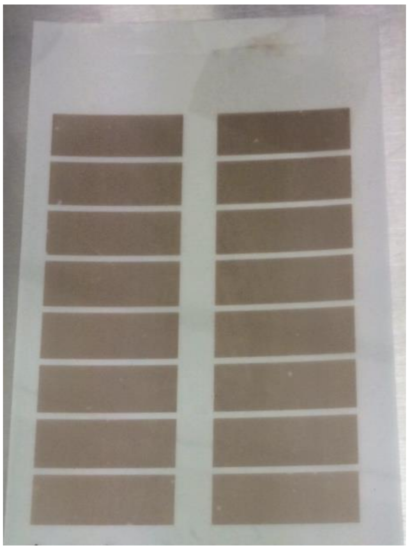


Figure 4.15: Proofed sample.

BH looper

Figure 4.16: BH Looper

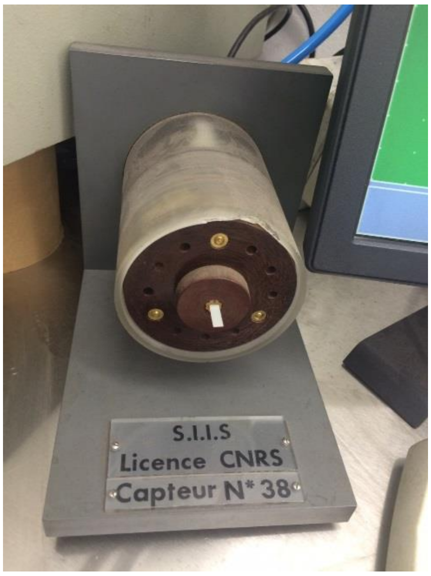


Figure 4.17: BH Looper sensor head.

4.4.2 Materials

The formulations considered involve the materials presented in Table 4.8 (Actual formulations and further information are available in Appendix 2).

Table 4.8: Materials used in formulations.

HL0104	HL0301
IPAC	*MEK*
1540A	*Rhodafac RE/610E*
Rhodafac RE/610E	*Lecithin*
Lecithin	*Alumina E330*
BYK-070	*Magnetite MO4232*
Alumina E330	*MaghemiteMO2228HC*
Magnetite MO4232	*UAGH-1*
Maghemite MO2228	*Resin HR01*
Resin AR01	

The milling time was varied between 5 and 60 minutes. The media used were either ceramic or stainless steel balls.

4.4.3 Formulation of HL0104 at Laboratory Scale

The solvent IPAC and 1540A were added to the vessel containing the media and mixed by the mini mixer mill for 30 seconds. Rhodafac RE/610E, Lecithin, BYK-070 and Alumina E330 were also added to the vessel which was mixed for more 30 seconds. The pigments Magnetite MO4232 and Maghemite MO2228 with IPAC were aggregated to the mixture and was mixed for the milling time of 5 minutes. The resin was added and mixed further for 15 minutes.

4.4.4 Formulation of HL0301 at Laboratory Scale

The solvent MEK, Rhodafac RE/610E, Lecithin and Alumina E330 were added to the sample vessel with the media and mixed by the mini mixer mill for 30 seconds. Following this, the pigment Magnetite MO4232 was put together in the sample and mixed further for 30 seconds. After this, Maghemite MO2228HC joined the process and the sample was mixed for 5 minutes. The resin was added and mixed further for 15 minutes.

4.4.5 Formulation of HL0104 and HL0301 at Pilot Scale.

The formulations were scaled up to pilot level. The formulation and production took place at BBP. The micro attritor allows a scale of 0.25 L solvent and uses a circular paddle for mixing in steel media and the milling times of 1, 2 and 4 hours.

The mini attritor refers to a scale of 1.0 L and used two different paddles, the one labelled as R refers to a circular paddle and the one labelled as A refers to an s-attritor paddle. The Mini-R had the milling times of 2 and 4 hours and the Mini-A the milling times of 1 and 2 hours.

4.4.6 Formulation of HL0104 and HL0301 at Production Scale.

Formulations were also completed on 30s attritor (80 kg batches) and the 60s attritor (160 kg batches) by the production team in HMI, and then subjected to analysis.

4.5 Formulation Results and Discussion

4.5.1 Laboratory Scale Analyses

Multiple formulations of HL0104 and HL0301 were created as above to observe particular trends and relationships present. The relationship between milling time and coercivity, squareness or SF_D for both ceramic and steel media are depicted in the figures 4.18 to 4.24.

HL0104:

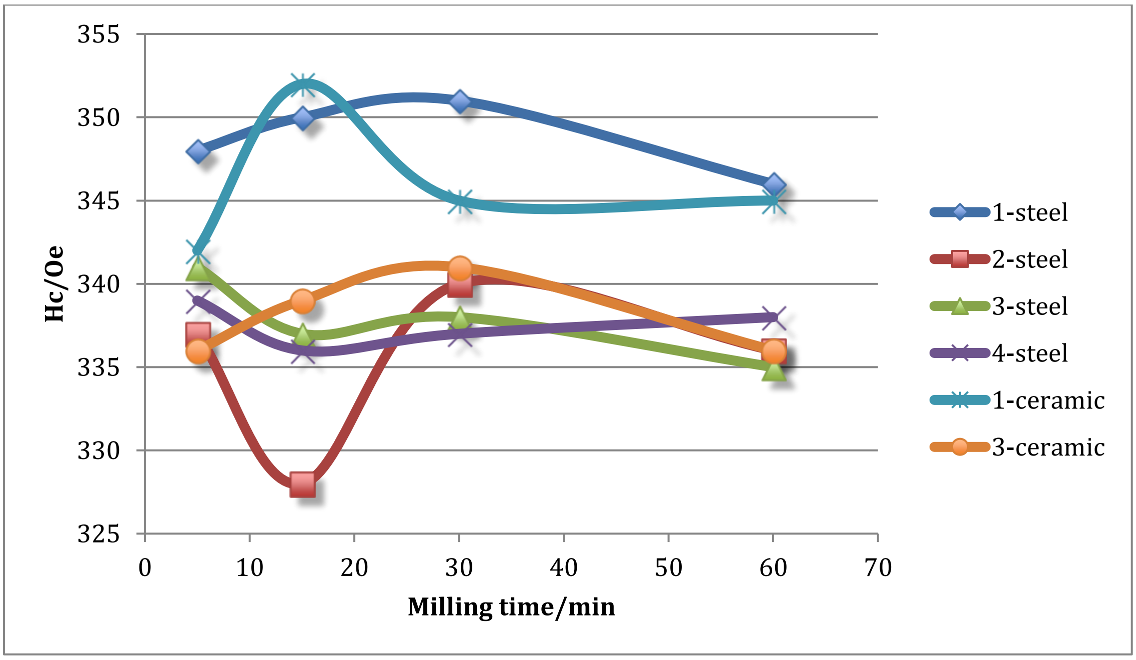


Figure 4.18: Hc vs Milling time HL0104 (the lines are drawn to guide the eye).

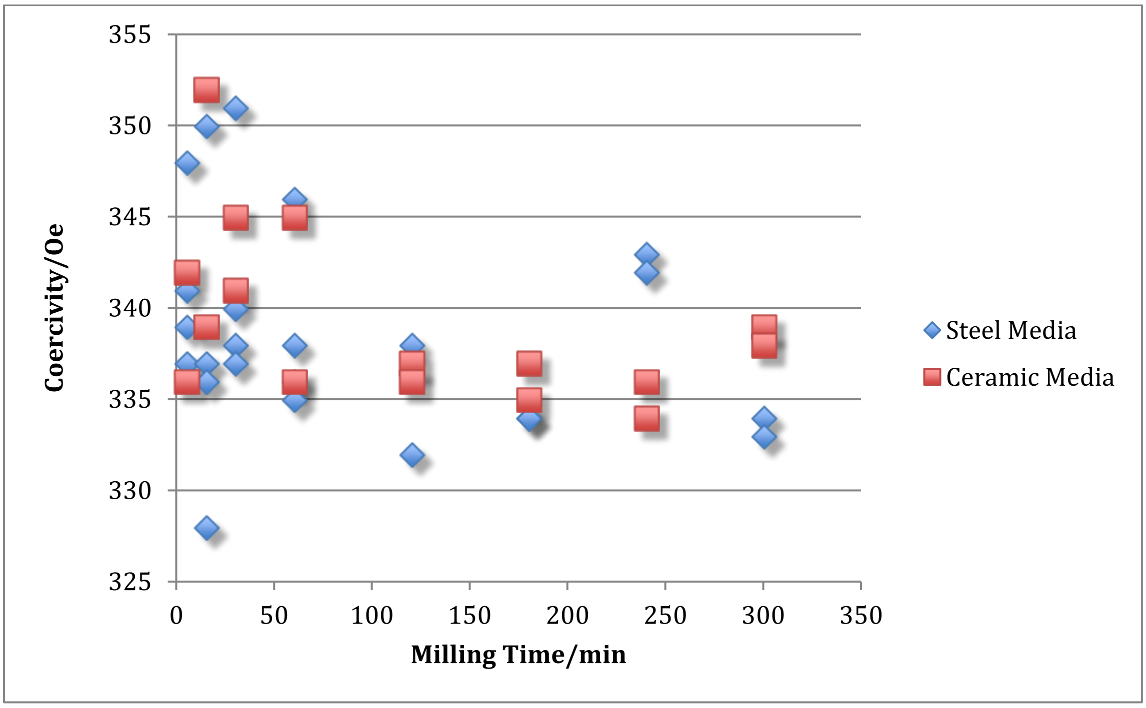


Figure 4.19: Hc vs. Milling time for a prolonged period for HL0104.

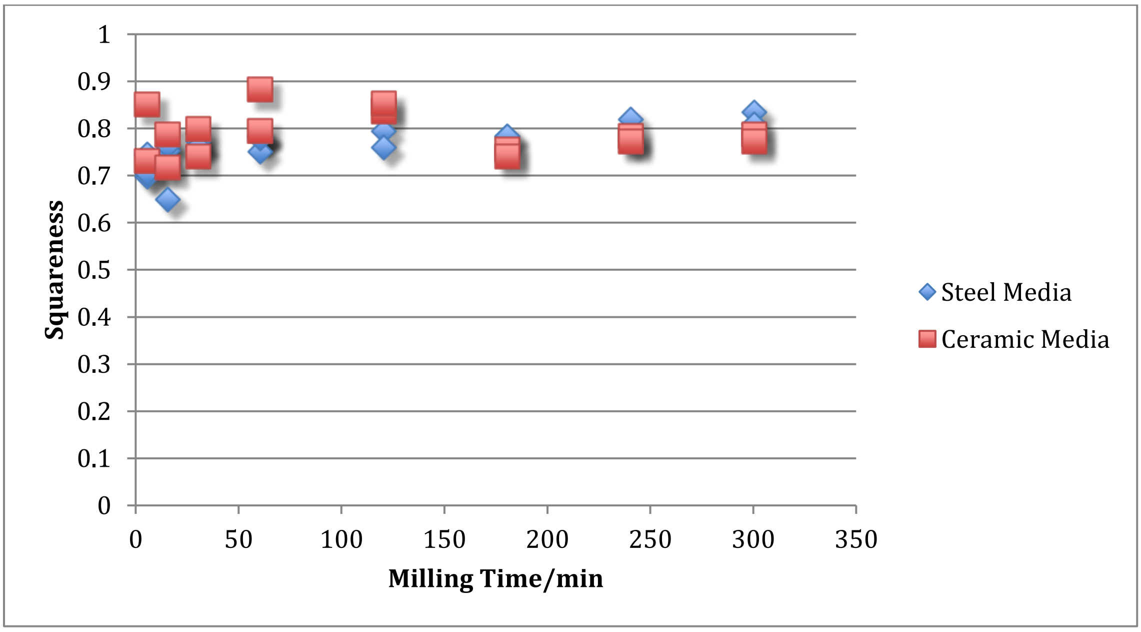


Figure 4.20: Squareness vs. Milling time for HL0104.

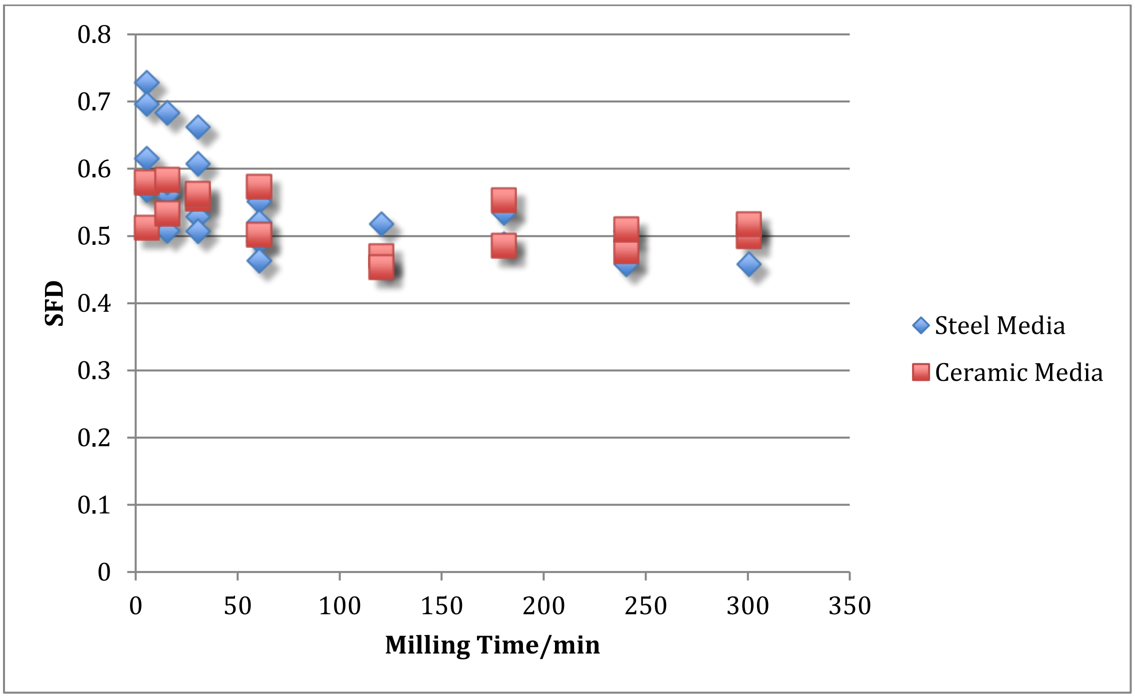


Figure 4.21: SF_D vs. Milling time for HL0104.

<u>HL0301:</u>

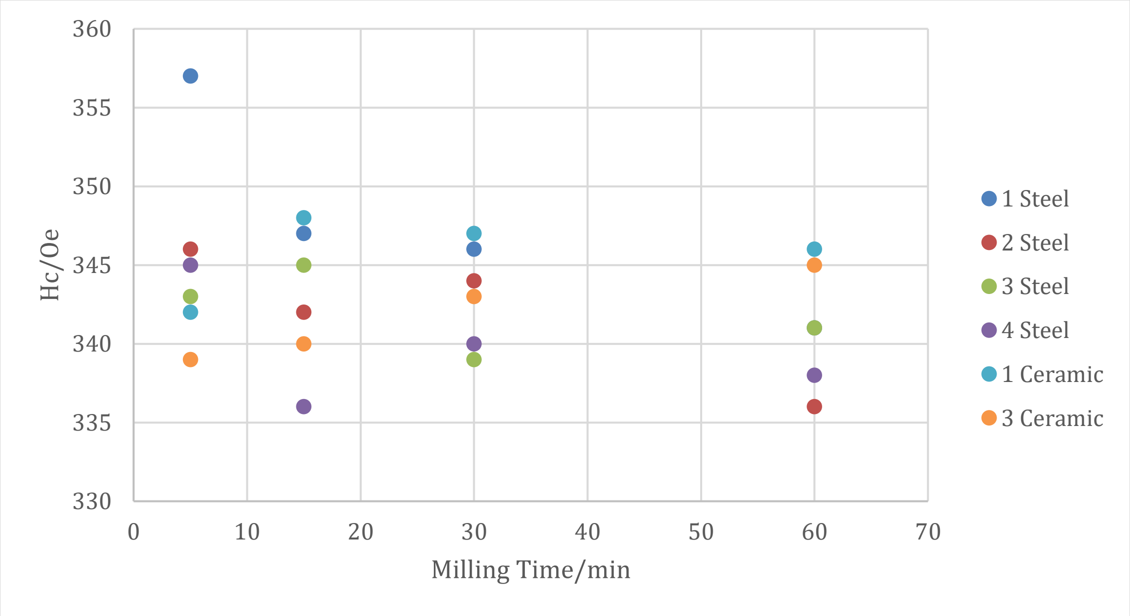


Figure 4.22: Hc vs. Milling time for HL0301.

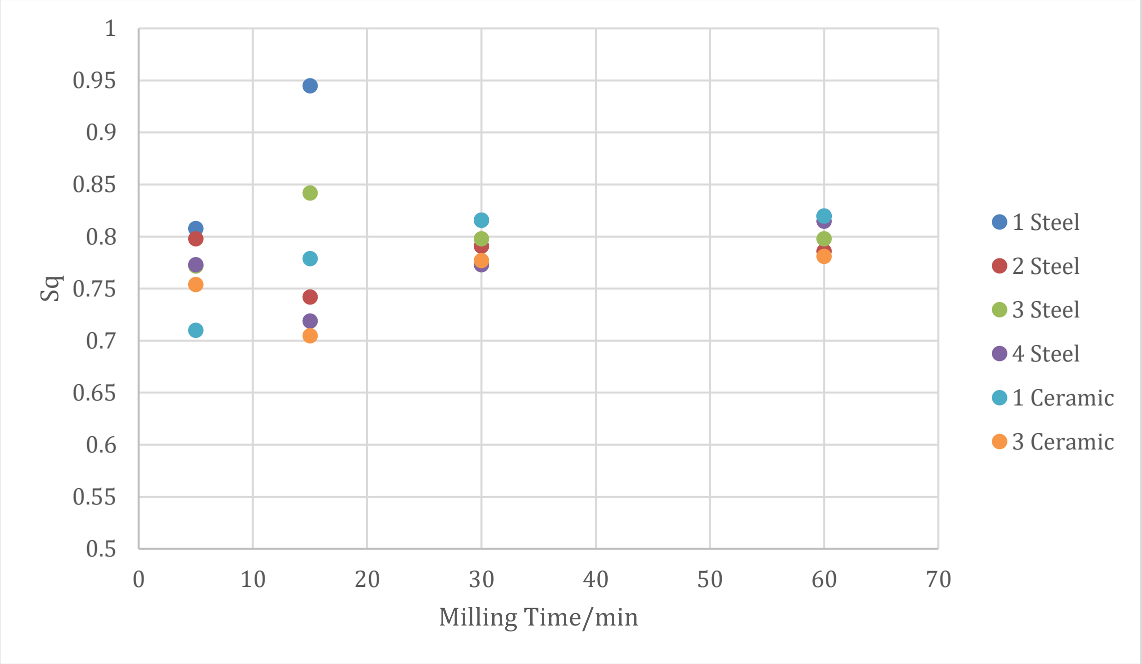


Figure 4.23: Squareness vs. Milling time for HL0301.

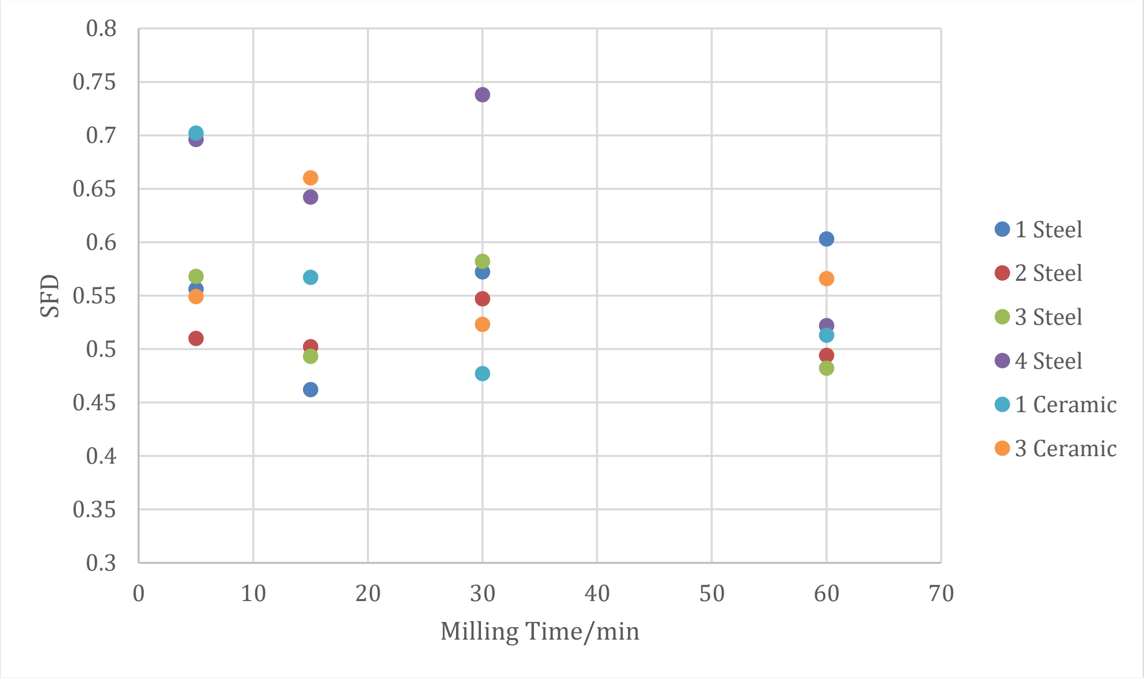


Figure 4.24: SF_D vs. Milling time for HL0301.

Interpretation

Coercivity decreases with milling time by approximately 50 Oe in the 0-300 minute range for HL0104/HL0301. This is more apparent when using steel media rather than ceramic. Squareness increases with milling time by approximately 0.12 in this period, and again this occurs more so for steel media than ceramic. SF_D decreases with milling time by approximately 0.25 using steel, or approximately 0.1 using ceramic in the 0-300 minute range. Viscosity generally decreases with milling time in the 0-60 minute range.

4.5.2 Pilot Scale Analyses

It is pertinent to understand the translation of the trends observed on a laboratory scale to a larger pilot scale, so that an indication of how changing parameters will affect the formulation at production scale.

Milling Time:

Two pilot scales were explored through the use of the micro and mini attritors and the effect of coercivity, squareness, SF_D and viscosity in comparison with milling time for the HL0104 formulation are recorded in figures 4.25 to 4.28.

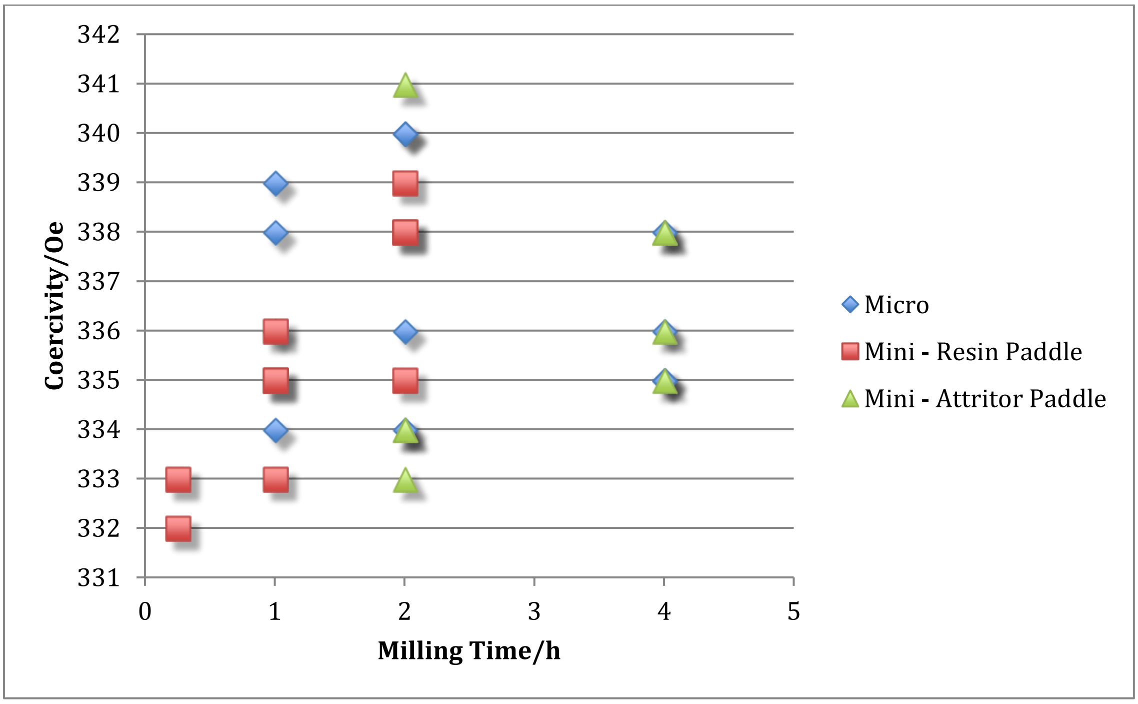


Figure 4.25: Hc vs. Milling Time for HL0104.

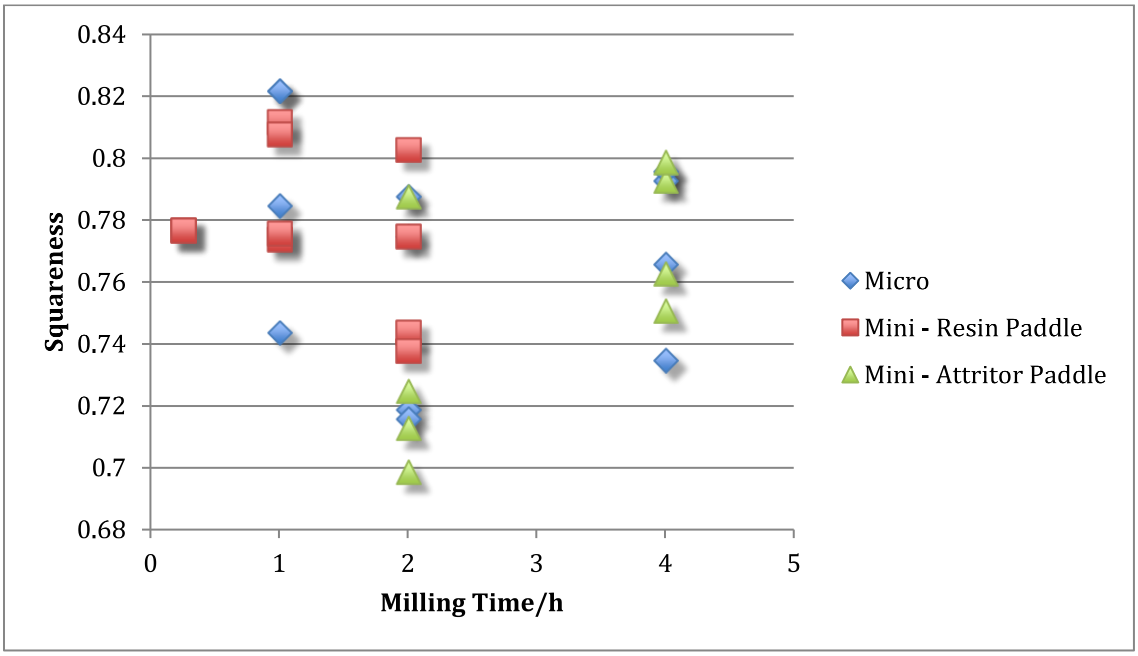


Figure 4.26: Squareness vs. Milling Time for HL0104.

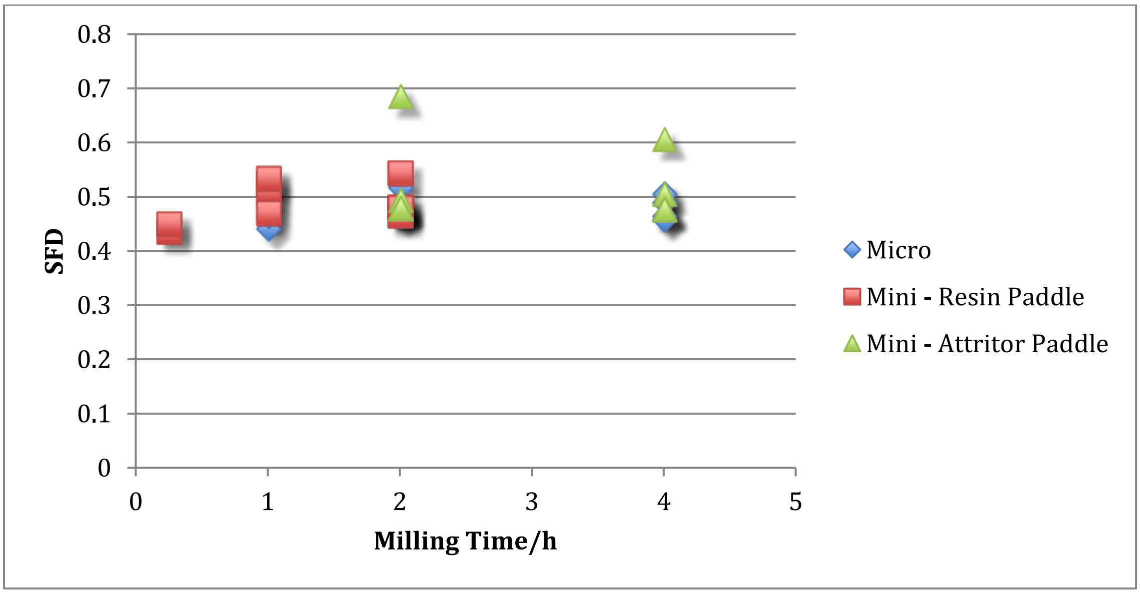


Figure 4.27: SF_D vs. Milling Time for HL0104.

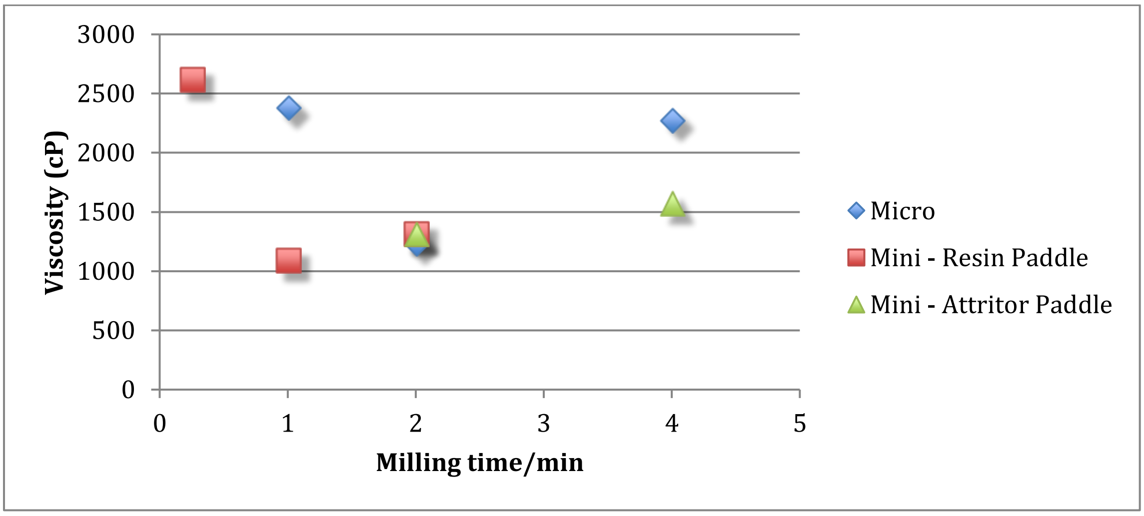


Figure 4.28: Viscosity vs. Milling Time for HL0104.

Interpretation

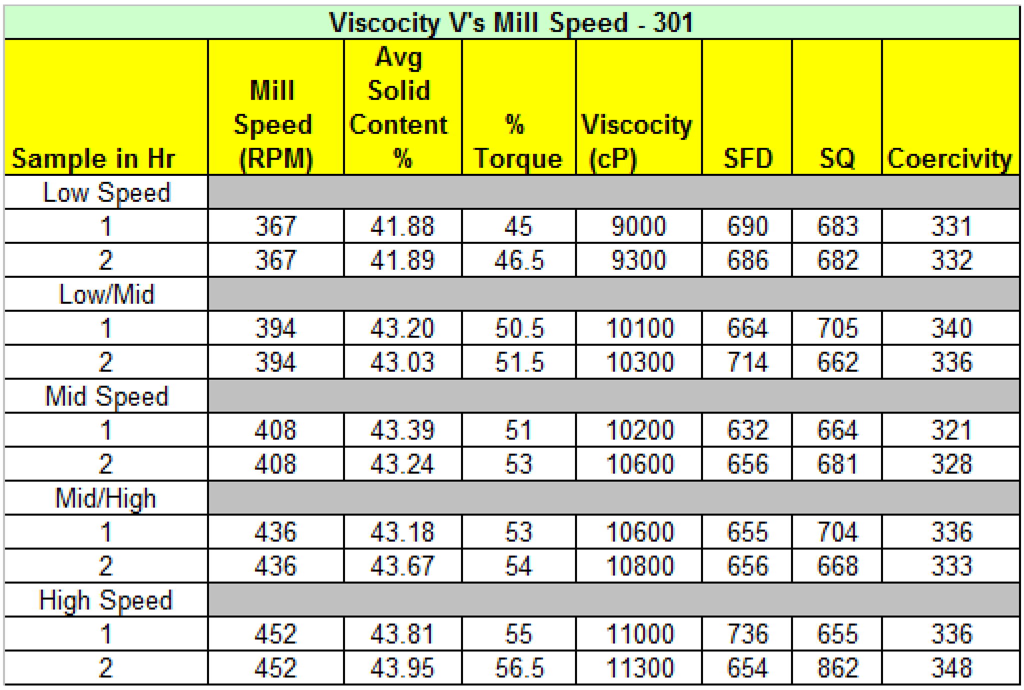
The micro attritor uses a circular paddle for mixing the components in steel media whereas the mini attritor has both a circular paddle (mini-R) or an "S-type attritor paddle" (mini-A). All milling was undertaken using steel media rather than ceramic. Mini-R and Mini-A show little difference in effect on final ink properties, as do whether the formulation was made in a mini or micro attritor, except in points (3) and (4) below.

1. Coercivity is constant with milling time.
2. Squareness is constant with milling time.
3. SF_D increases with milling time (mini-R and micro), but decreases with milling time for mini-A
4. Viscosity is constant, but viscosities for micro are higher than for mini

<u>Milling Speed:</u>

The mini attritor was also adopted to test the effect of milling speed at a constant time against viscosity. Due to the gearing of the attritor, 367 rpm was the lowest speed possible, and was not entirely representative of full scale manufacturing, normally processed at 50-60 rpm. It will still be possible to determine a trend and interpolate the effects to larger scale manufacturing. Increments in mill speed whilst keeping all other factors constant, and performing a full quality assurance analysis of the final product, the direct effect on the final viscosity of the slurry was determined. Five individual batches were created with five different mill speeds. Results can be seen below in Table 4.9.

Table 4.9: Viscosity vs mill speed data for HL0301.



Viscocity V's Mill Speed - 301							
Sample in Hr	**Mill Speed (RPM)**	**Avg Solid Content %**	**% Torque**	**Viscocity (cP)**	**SFD**	**SQ**	**Coercivity**
Low Speed							
1	367	41.88	45	9000	690	683	331
2	367	41.89	46.5	9300	686	682	332
Low/Mid							
1	394	43.20	50.5	10100	664	705	340
2	394	43.03	51.5	10300	714	662	336
Mid Speed							
1	408	43.39	51	10200	632	664	321
2	408	43.24	53	10600	656	681	328
Mid/High							
1	436	43.18	53	10600	655	704	336
2	436	43.67	54	10800	656	668	333
High Speed							
1	452	43.81	55	11000	736	655	336
2	452	43.95	56.5	11300	654	862	348

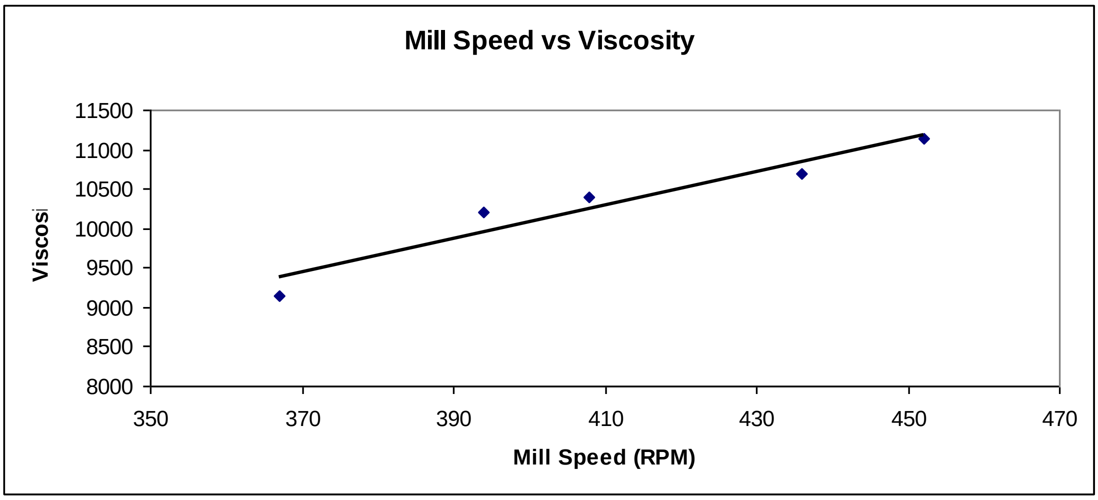


Figure 4.29: Milling Speed vs Viscosity (in cP units).

Interpretation

Figure 4.29 represents a linear correlation between mill speed and viscosity. The observed effect is an increase in viscosity with a higher mill speed at a constant time and solid content. As with the milling time and viscosity investigation, this is an expected effect due to the increased energy input into the ink.

Wetting Agent Levels:

Wetting agents are added to magnetic ink to encourage and maintain equal dispersion of all pigment particles. Alterations to the amount of surfactant within the formulation affects both ink performance under coating and other factors such as viscosity. The usual wetting agent level in a magnetic ink formulation is 2% per pigment volume. In this experiment five individual scaled down batches were produced with a variation in wetting agent percentage of 0-4% with respect to pigment volume. As previously, a full quality assurance analysis was undertaken on the sample batches to ensure constant parameters other than the independent variable.

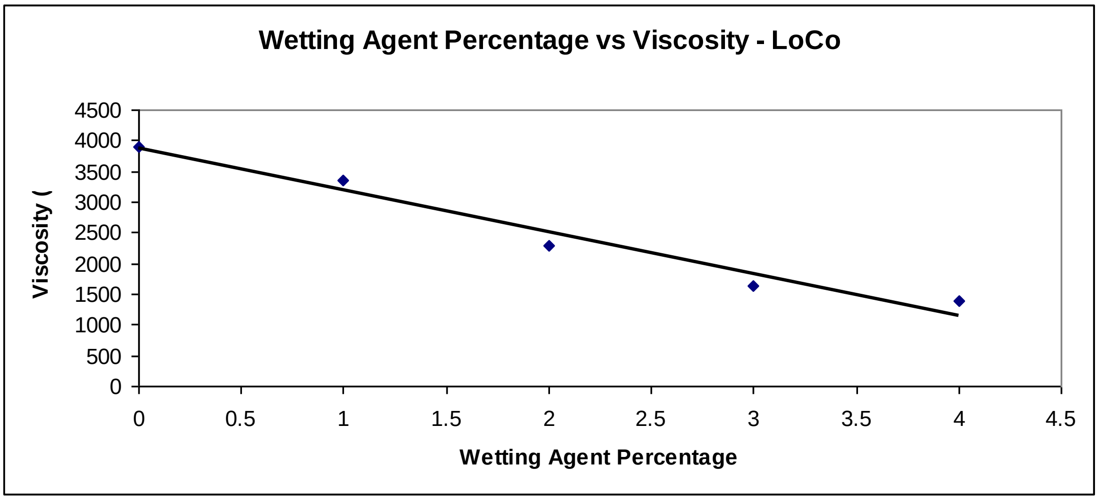


Figure 4.30: Wetting agent percentage vs Viscosity for LoCo slurry (in cP units).

Interpretation

Figure 4.30 demonstrates a linear correlation between wetting agent percentage in relation to pigment volume and the corresponding viscosity value. As the level of wetting agent is increased, the viscosity of the slurry becomes lower. This is attributable to a lowering in interfacial tension between particles and solvent. Approximately 2% wetting agent gives the ideal conditions for slurry manufacture and processing as seen in figure 26.

4.5.3 Production Scale Results

To confirm findings at both lab and pilot scales, samples of both HL0104 and HL0301 were taken from various production batches in the HMI facility to study the effect of milling time (shown in figures 4.31 to 4.34). Other relationships are observed in figures 4.35 to 4.37.

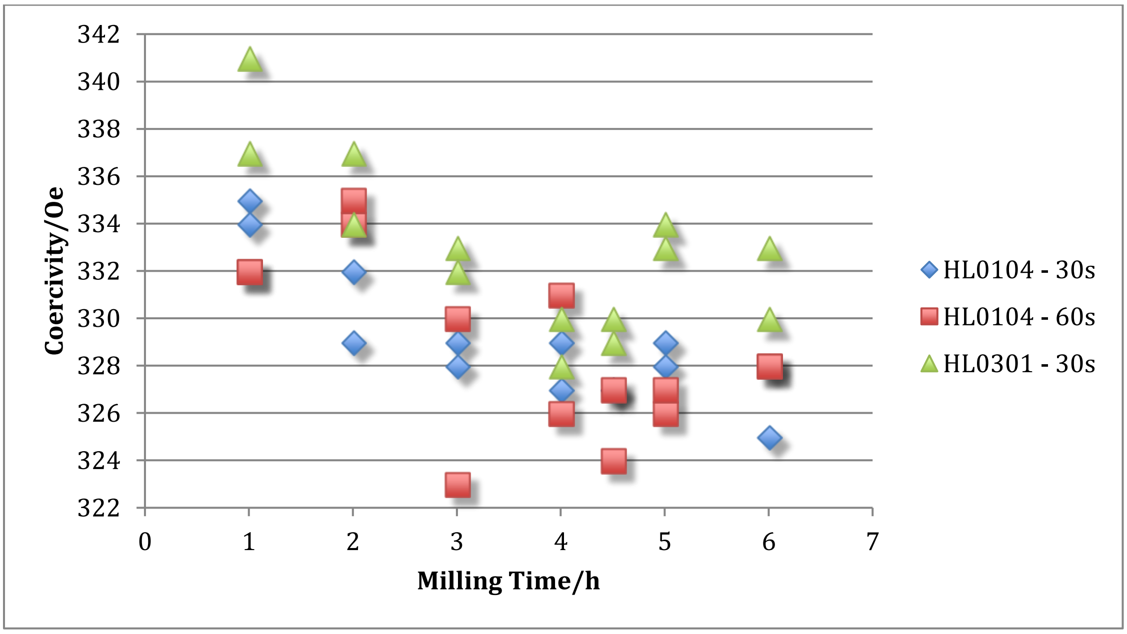


Figure 4.31: Coercivity vs. milling time at production scale.

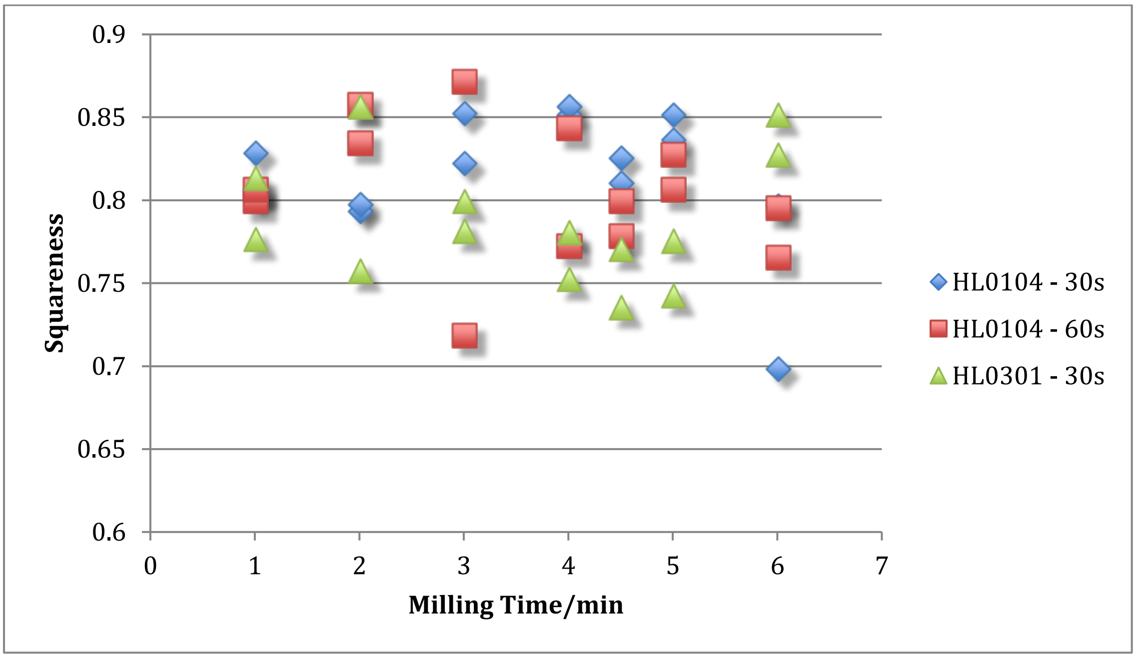


Figure 4.32: Squareness vs. milling time at production scale.

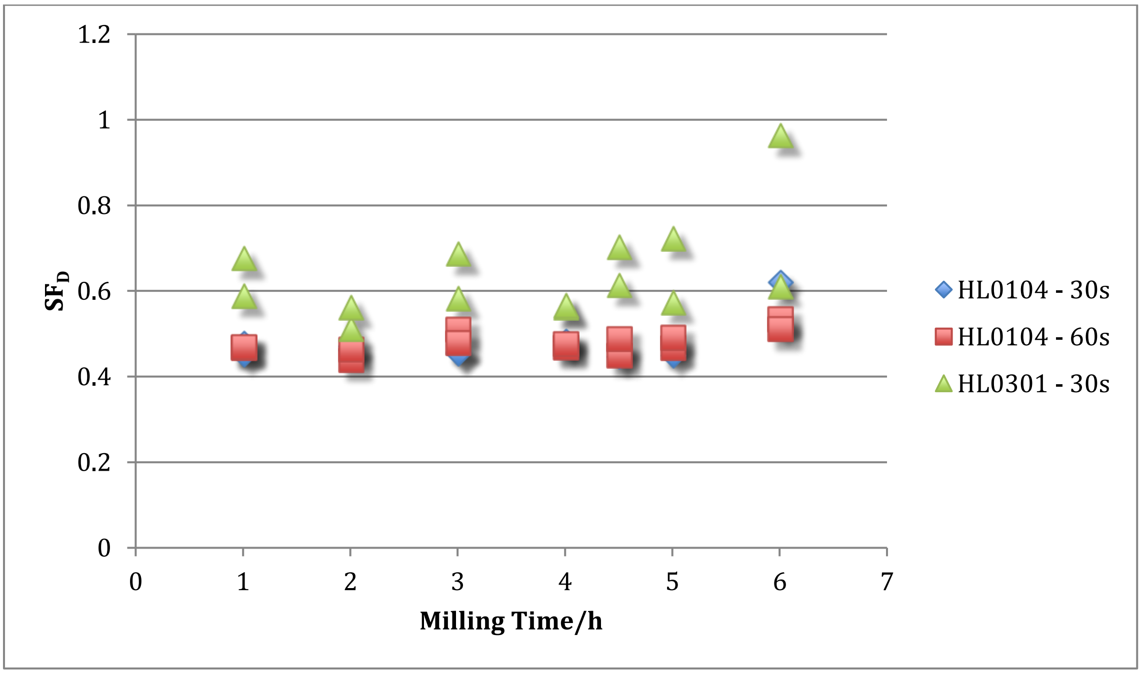


Figure 4.33: SF_D vs. milling time at production scale.

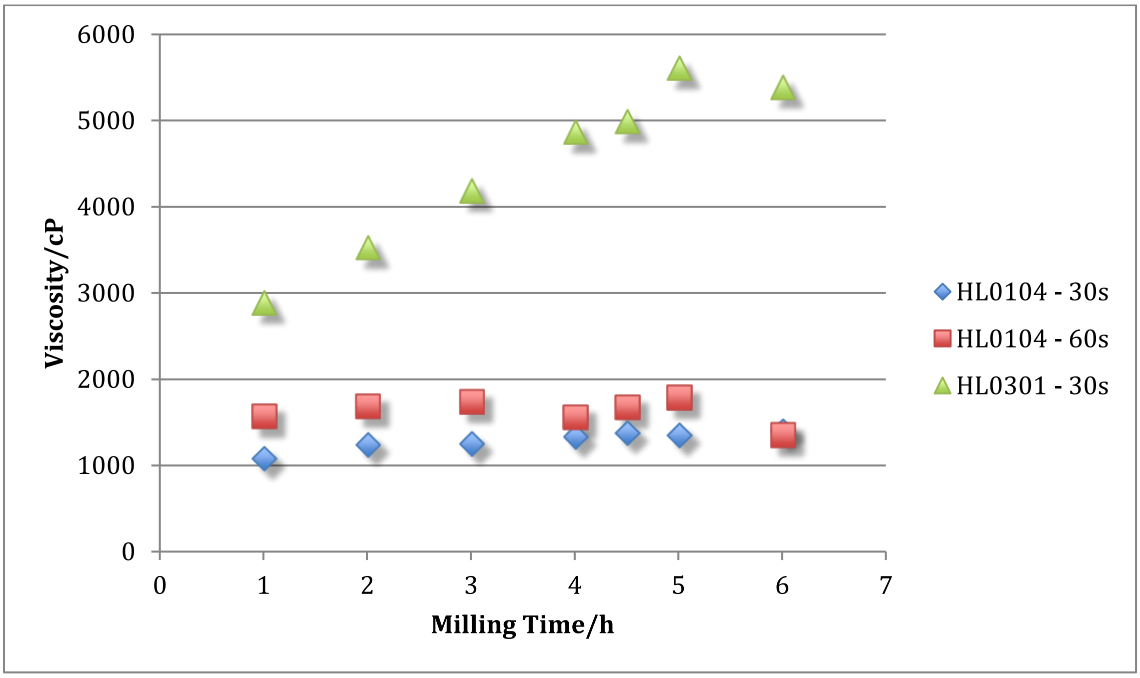


Figure 4.34: Viscosity vs. milling time at production scale.

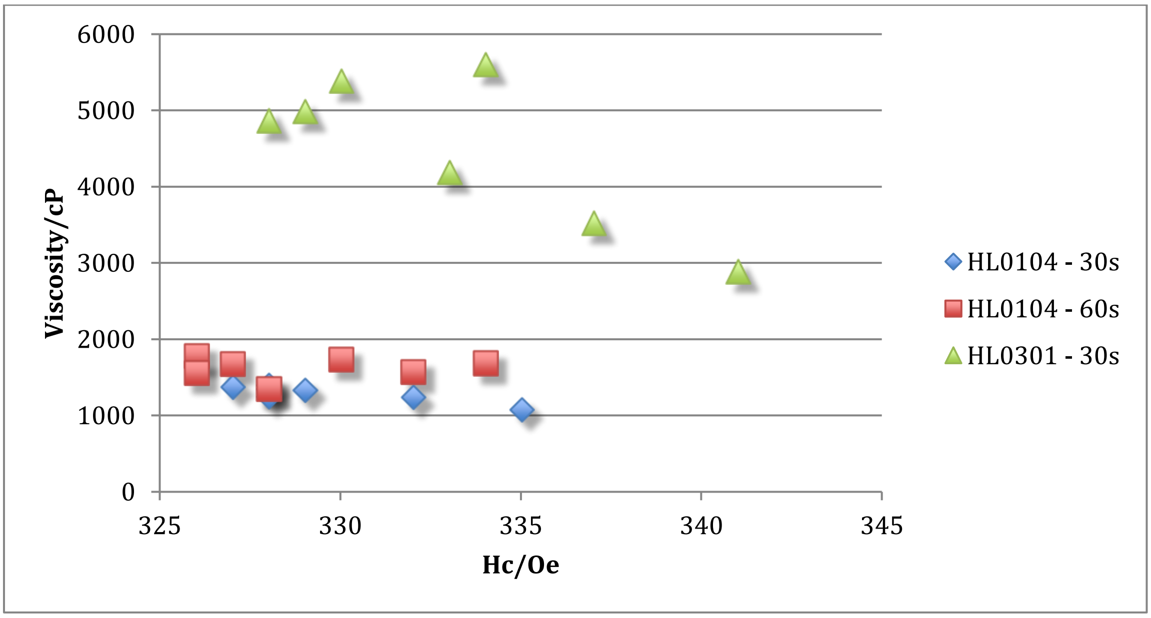


Figure 4.35: Coercivity vs. viscosity at production scale.

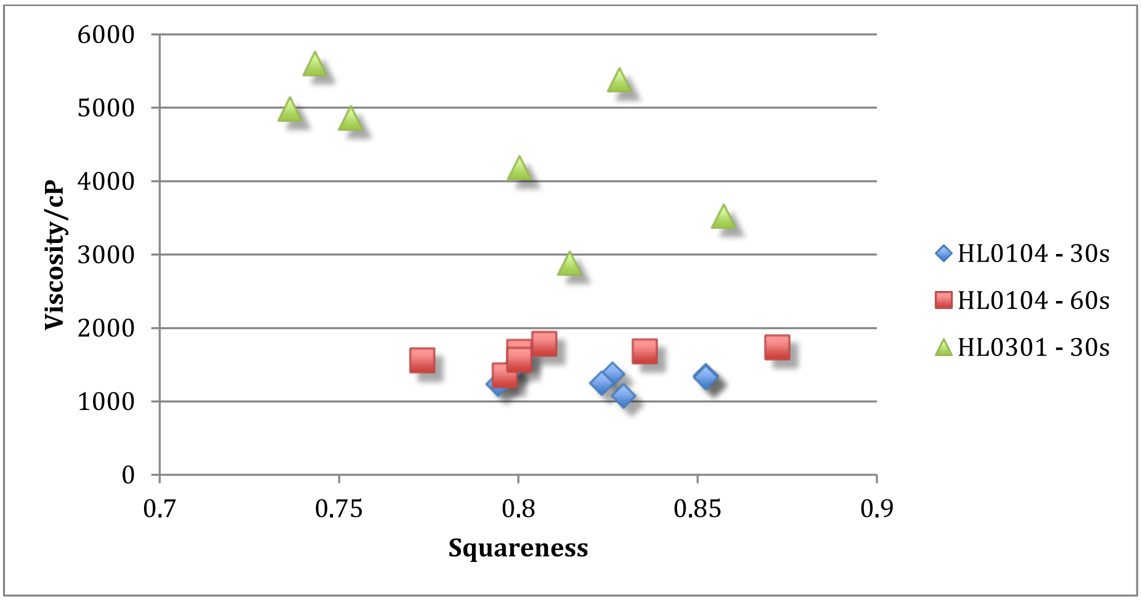


Figure 4.36: Viscosity vs. squareness at production scale.

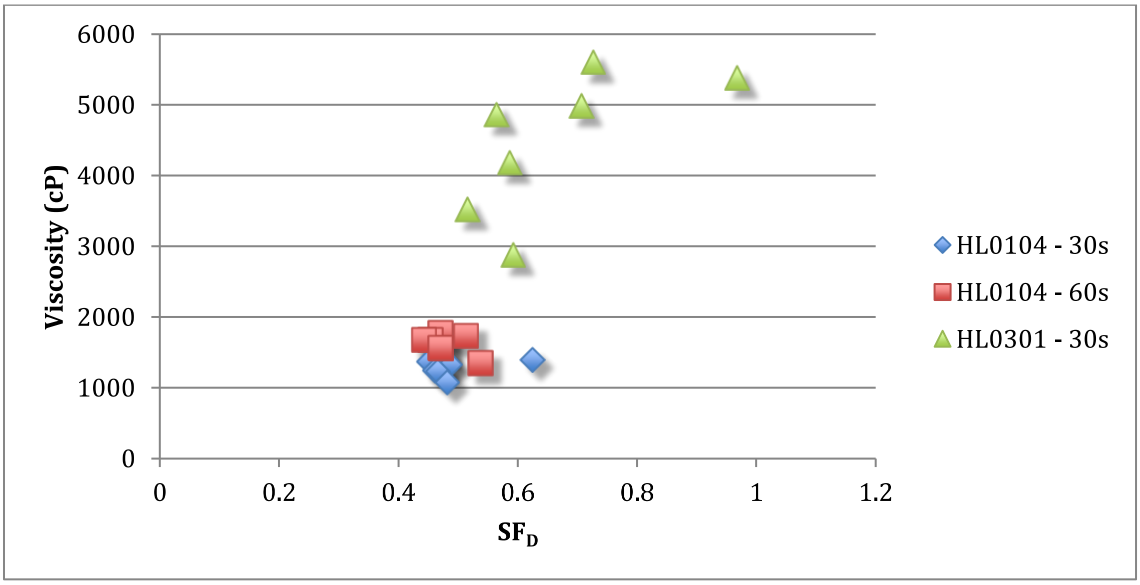


Figure 4.37: Viscosity vs. SF_D at production scale.

Interpretation

Two types of attritor were used to make the formulations in production for assessment. These are the- 30s and 60s machines - both adopt an "S-type attritor paddle". 30s attritor batch size is 80 kg (25 L solvent). 60s attritor batch size is 160 kg (55 L solvent). The following observations were made:

1. Coercivity decreases as milling time increases (small difference observed in results

between 30s and 60s; a higher coercivity was obtained for HL0301 *vs.* HL0104)
2. Squareness goes through a maximum at 3 hours (60s) or 4 hours (30s) for HL0104 but stays constant for HL0301 until the resin is added, when it increases.
3. SF_D is constant and independent of attritor size (HL0104), but increases after resin is added for both HL0104 and HL0301. SF_D is higher for HL0301 than for HL0104.
4. Viscosity increases as milling time increases, with HL0104 made in the 60s showing a viscosity greater than HL0104 made in the 30s. Viscosity decreases as coercivity increases.
5. Solid content increases as milling time increases, likely to be as a result of solvent evaporation!

Having characterized the formulation process, in the next chapter, the practical design considerations of the process plant are discussed.

References

[1] J. M. Coulson, J. F. Richardson, *Chemical Engineering – Particle Technology and Separation Processes*, 2002, **2**, 1-1183.
[2] Göktürk H., Maki K., *Journal of Magnetism and Magnetic Materials,* 1996, **154**, 279-290.

Chapter 5 – Process Plant Design for Ink Manufacture

5.1 Process Room Design

The HMI Process Room was designed to contain a manufacturing process handling chemicals with various hazards. Once raw materials were selected and initial formulations were developed, the nature of the products required for full scale manufacture were clear. In order to understand the hazards of each of the compounds required, the Safety Data Sheets for each material component were studied. Each of the material hazards are listed in Chapter 1 (through the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) symbols).

A specialist area within the BBP factory was selected and created so that it could operate as a dedicated, standalone function within the daily business activities, with easy access to the loading bays.

The selected area was created with through the erection of concrete block walls. As demonstrated in figure 5.1. An annex laboratory and raw materials cage were designed and constructed as per figure 5.2.

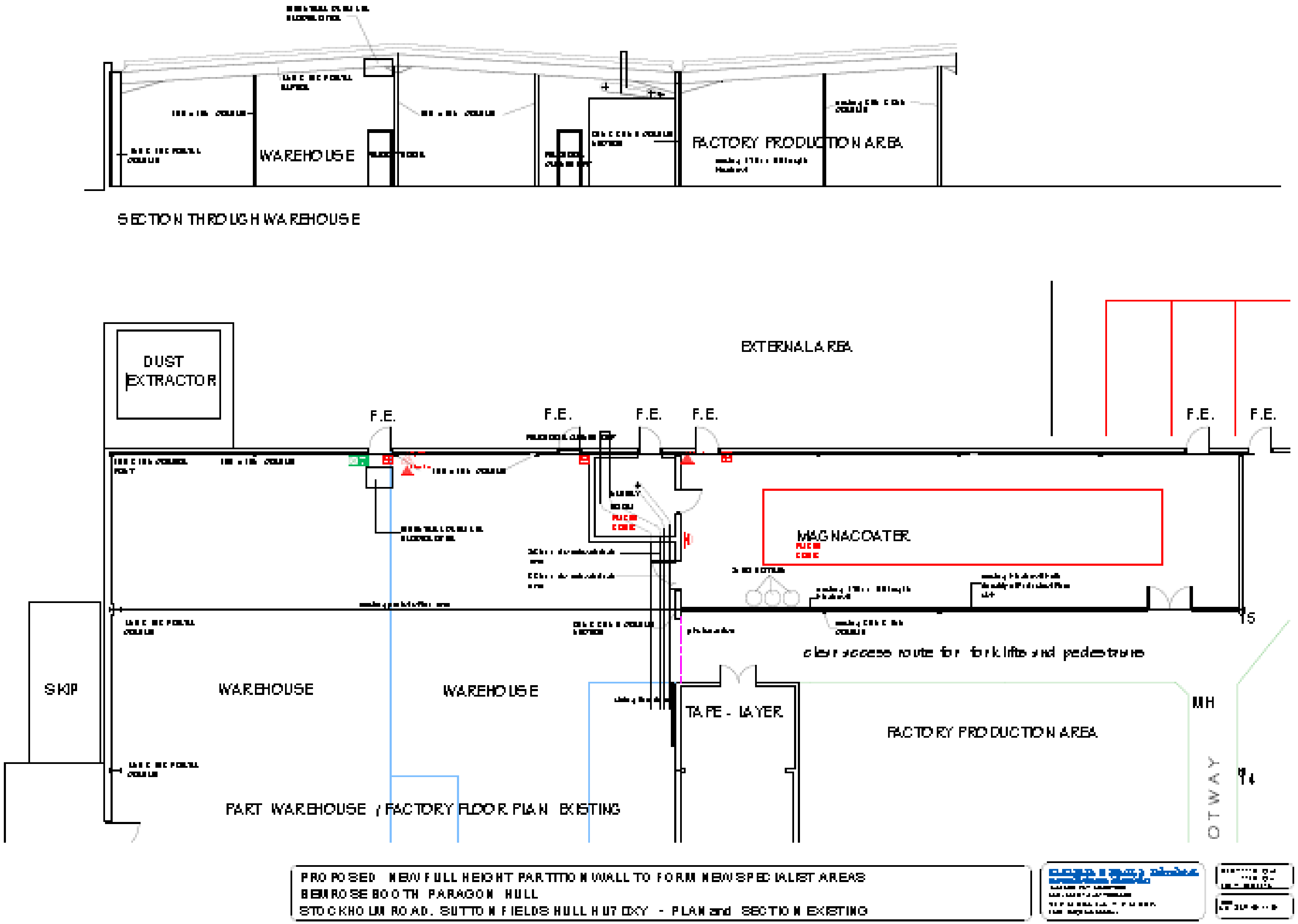


Figure 5.1: Dedicated site area for HMI Process Room Build.

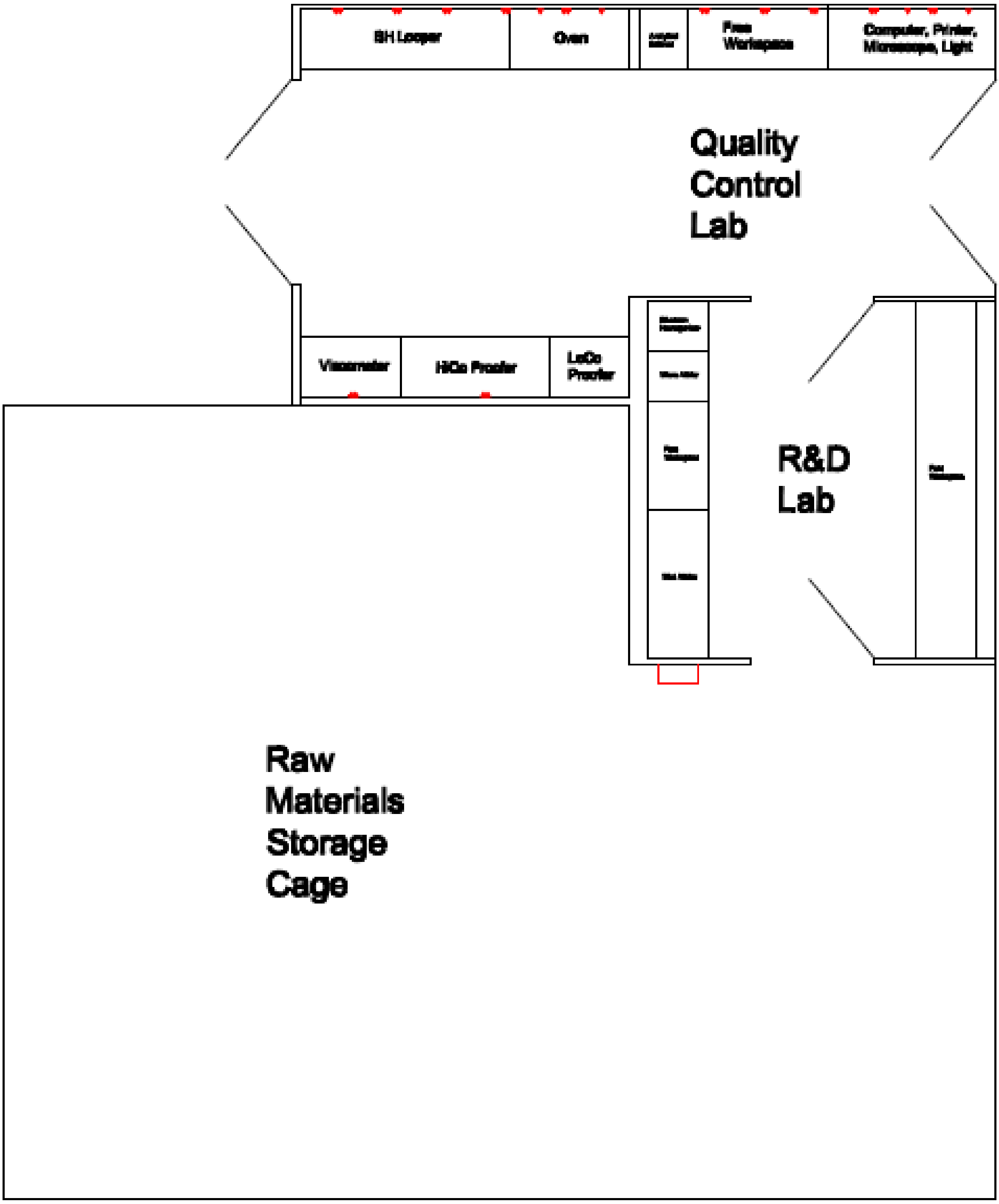


Figure 5.2: Annex laboratory and raw materials cage for HMI Process

The use of large volumes of organic solvents in any chemical manufacturing process is hazardous, in particular owing to the possible formation of vapour cloud explosions. Explosive atmospheres can be caused by flammable gases, mists or vapours or by combustible dusts. If the correct level of air and substance present, a source of ignition to could cause an explosion. There are many ways to mitigate this risk including prevention of releases of dangerous substances, which can create explosive atmospheres, and preventing sources of ignition.

The Dangerous Substances and Explosive Atmospheres Regulations 2002 (DSEAR) place duties on employers to eliminate or control the risks from explosive atmospheres in the workplace. Under DSEAR, an explosive atmosphere is defined as a mixture of dangerous substances with air, under atmospheric conditions, in the form of gases, vapours, mist or dust in which, after ignition has occurred, combustion spreads to the entire unburned mixture. Atmospheric conditions are commonly referred to as ambient temperatures and pressures, *i.e.* temperatures of –20°C to 40°C and pressures of 0.8 to 1.1 bar.

ATEX is the name commonly given to the two European Directives for controlling explosive atmospheres:

1) Directive 99/92/EC (also known as 'ATEX 137' or the 'ATEX Workplace Directive') on minimum requirements for improving the health and safety protection of workers potentially at risk from explosive atmospheres.

2) Directive 94/9/EC (also known as 'ATEX 95' or 'the ATEX Equipment Directive') on the approximation of the laws of Members States concerning equipment and protective systems intended for use in potentially explosive atmospheres.

Based upon machine capacity and the chosen processing method, the major identified hazards were the flammable class 3 volatile organic solvents and the iron oxide dust. Due to the quantity of these substances the process build would need to be compliant under both EU ATEX Directives, but only for solvent processing and not dust.

In Great Britain, the requirements of Directive 99/92/EC were put into effect through regulations 7 and 11 of the Dangerous Substances and Explosive Atmospheres Regulations 2002 (DSEAR). The requirements in DSEAR apply to most workplaces where a potentially explosive atmosphere may occur, and require the control or elimination of risks from dangerous substances.

Areas where hazardous explosive atmospheres may occur into zones. The classification given to a particular zone, and its size and location, depends on the likelihood of an explosive atmosphere occurring and its potential persistence.

Areas classified into zones must be protected from sources of ignition. Equipment and protective systems intended to be used in zoned areas should be selected to meet the requirements of the Equipment and Protective Systems Intended for Use in Potentially Explosive Atmospheres Regulations 1996. Equipment already in use before July 2003 can continue to be used indefinitely provided a risk assessment shows it is safe to do so. Entry points to areas classified into zones must be marked with a specified 'EX' sign.

PPE (Personal Protective Equipment) that prevents an electrostatic discharge must be provided in zoned areas so as to prevent ignition of flammable substances, *e.g.* anti-static footwear. The clothing provided depends on the level of risk identified in the risk assessment.

Before a workplace containing zoned areas comes into operation for the first time, the employer must ensure that the overall explosion safety measures are confirmed (verified) as being safe. This must be done by a person or organisation competent to consider the particular risks in the workplace, and the adequacy of the explosion control and other measures put in place. This can be undertaken in the form or a DSEAR Report. The aim of Directive 94/9/EC is to allow the free trade of 'ATEX' equipment and protective systems within the EU by removing the need for separate testing and documentation for each Member State. In Great Britain, the requirements of the Directive were put into effect through BIS Equipment and Protective Systems Intended for Use in Potentially Explosive Atmospheres Regulations 1996 (SI 1996/192). The Regulations apply to all equipment intended for use in explosive atmospheres, whether electrical or mechanical, and also to protective systems.

Manufacturers/suppliers (or importers, if the manufacturers are outside the EU) must ensure that their products meet essential health and safety requirements and undergo appropriate conformity procedures. This usually involves testing and certification by a 'third-party' certification body (known as a Notified Body) but manufacturers/suppliers can 'self-certify' equipment intended to be used in less hazardous explosive atmospheres. Once certified, the equipment is marked by the 'EX' symbol to identify it as such.

Certification ensures that the equipment or protective system is fit for its intended purpose and that adequate information is supplied with it to ensure that it can be used safely.

The manufacturing vessels employed were S-Type batch attritors, capable of batch sizes between 80 kg to 320 kg. Their functionality is described in Figure 2.10. See figure 5.3 for an example of the attritor type chosen.

Figure 5.3: 30s Attritor at BBP.

A resin solution is manufactured in a different type of vessel and is later introduced into the attritors during the process. The resin machines are tanks with a continuously stirring high shear paddle. An example of a resin mixer can be seen in figure 5.4.

Figure 5.4: Resin mixer at BBP.

A Process Flow Diagram was created for the process that incorporates the use of these machines is illustrated in figure 5.5.

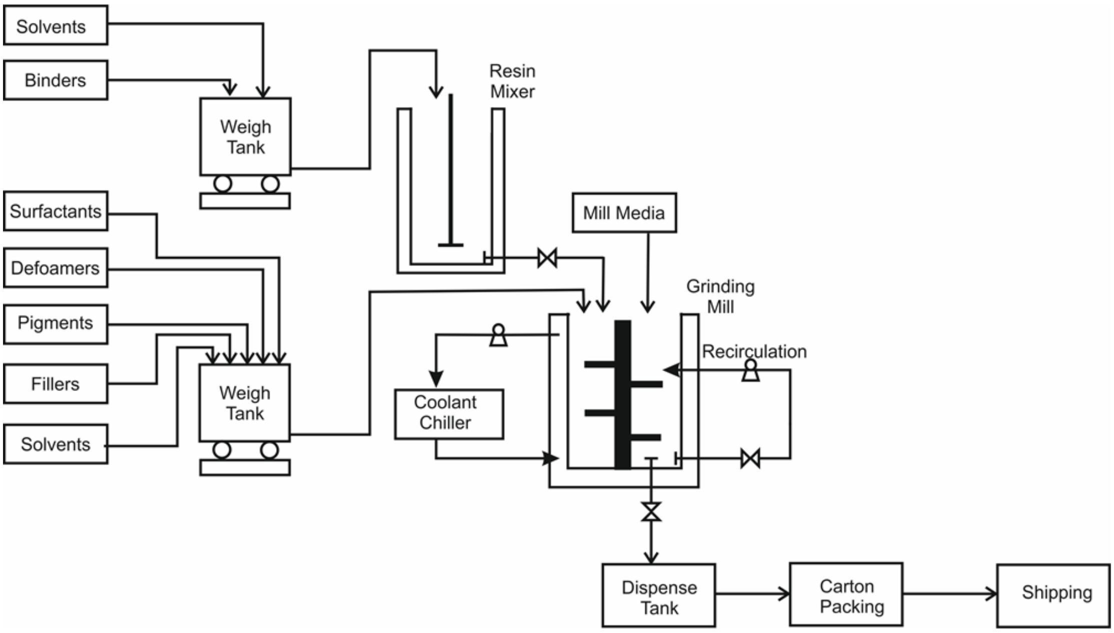


Figure 5.5: Process Flow Diagram for HMI.

The proposed HMI layout is depicted in figure 5.6, and the proposed machinery layout in figure 5.7.

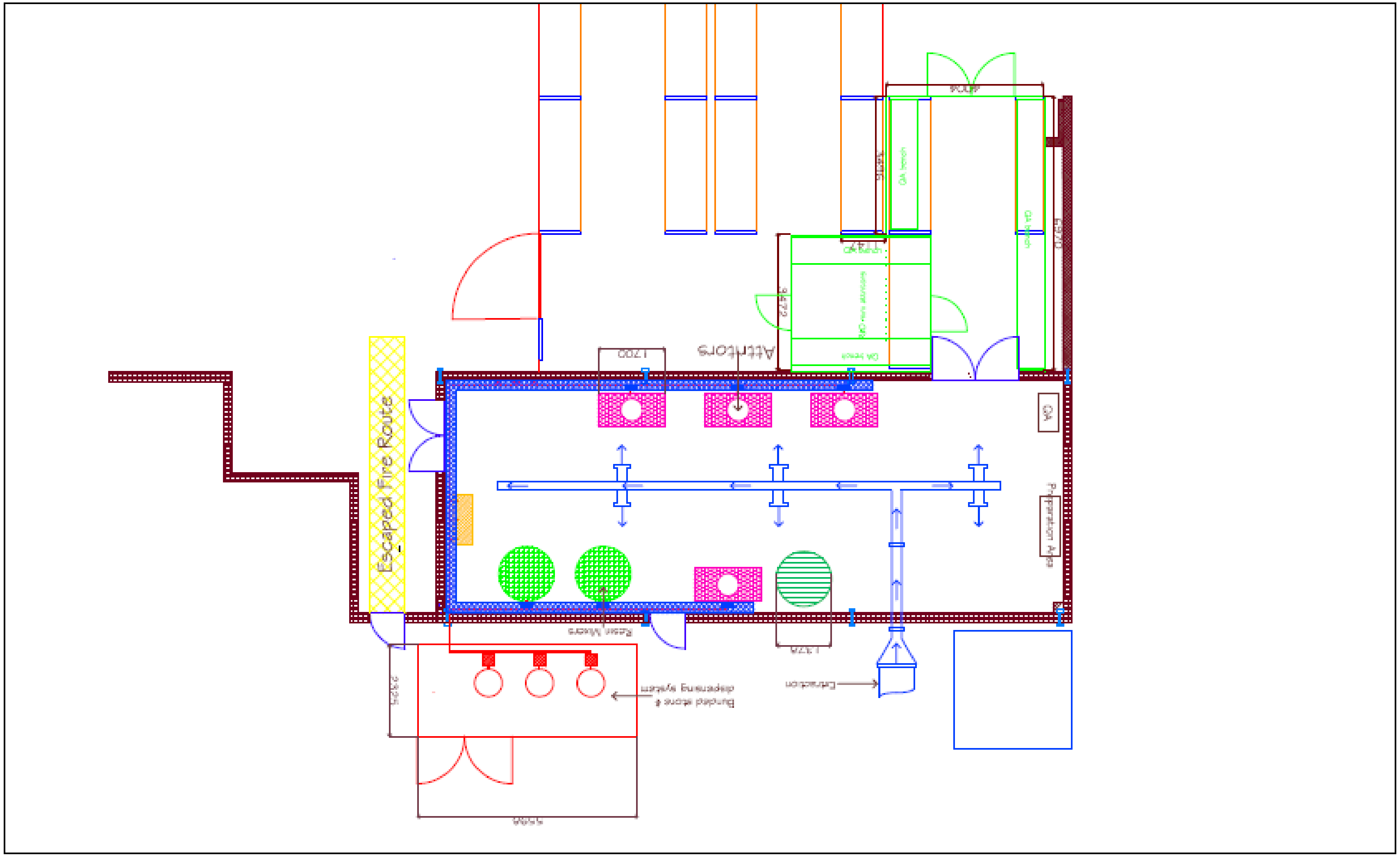


Figure 5.6: Proposed HMI layout.

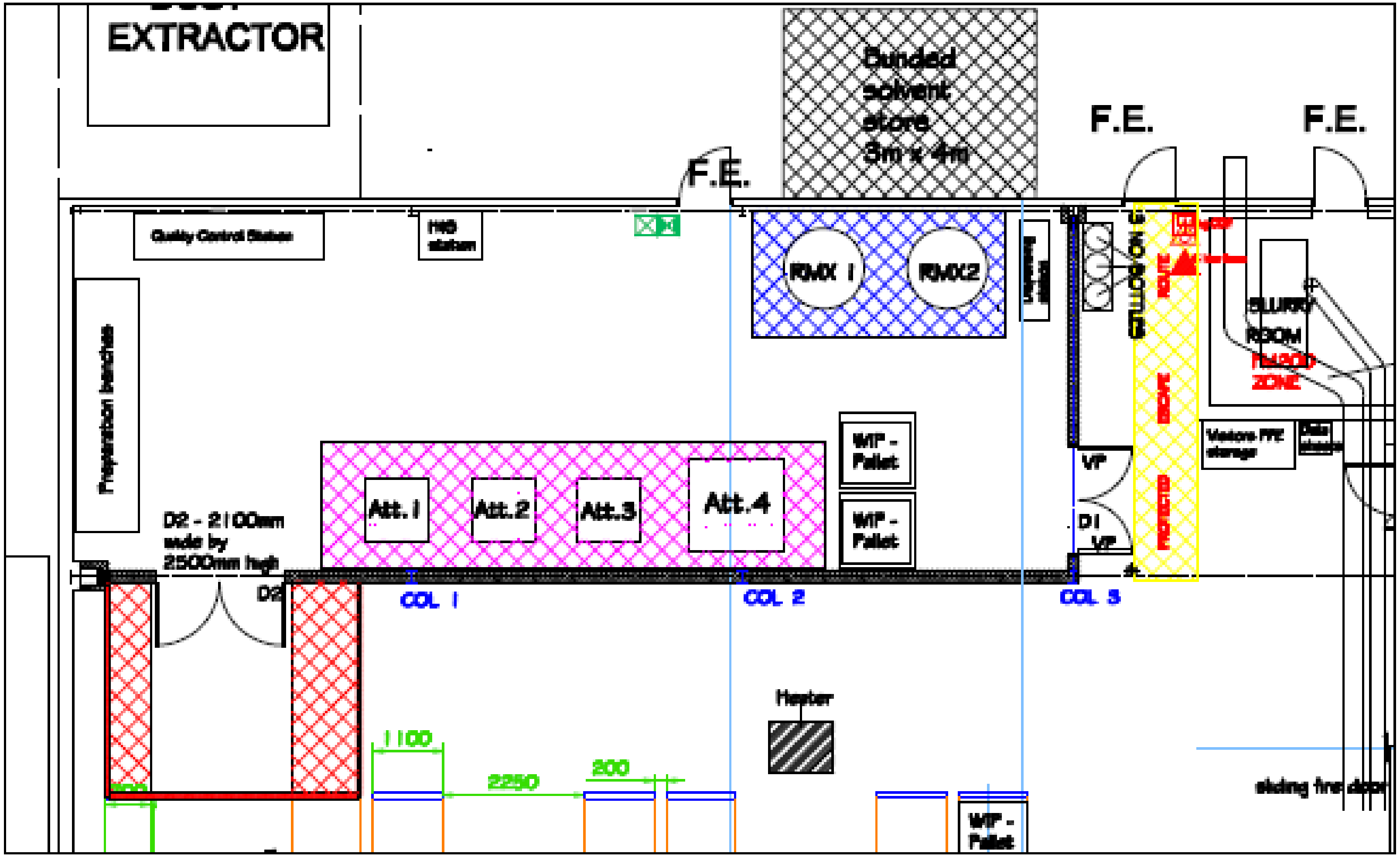


Figure 5.7: Proposed HMI Machinery layout.

The machines themselves needed to be installed through ATEX approved electrical systems. A 200 A 24-way distribution board was provided for the installation of Zone 1 ATEX approved machine controls, isolators and emergency stop system. The equipment listed in table 5.1 was installed

Isolators:

Table 5.1: Isolator types.

Category	**Model**	**Information**
Isolators	2 x 63 A Triple pole lockable isolators.	ATEX Zone 1, IP66, Weatherproof.
Emergency Stop	6 x Emergency stop button.	ATEX Zone 1
Soft Start	2 x Soft Start	ATEX Zone 1, 15 kW
Man Lifter	7 x Meter man lifter boom	ATEX Zone 1
Lighting	9 x 6 Series Ex de 620 Well Glass Range	250 W Metal halide, Ex de II GD IIC T2 – T6, IP66
Earthing	1 x Newson Gale Earth-Rite MULTIPOINT Static Earthing System	ATEX Zone 1
	1 x Sole-Mate ii Anti-Static Door Way Entry	EN ISO 20345 – 1 x 10^9 Ohm, 115-230 Vac, IP65

Solvent Management:

Due to the volume and hazardous nature of the solvents used in manufacturing, a dedicated solvent transfer system was implemented to avoid manual handling of solvent during manufacturing. Storage of solvents was considered so as to offer the upmost level of SHE whilst being as efficient as possible for the manufacturing process. A 20 foot container with an integrated bund was selected to install the solvent management pumps (as shown in figures 5.8 and 5.9. The solvents to be transferred were IPAC, MEK and THF.

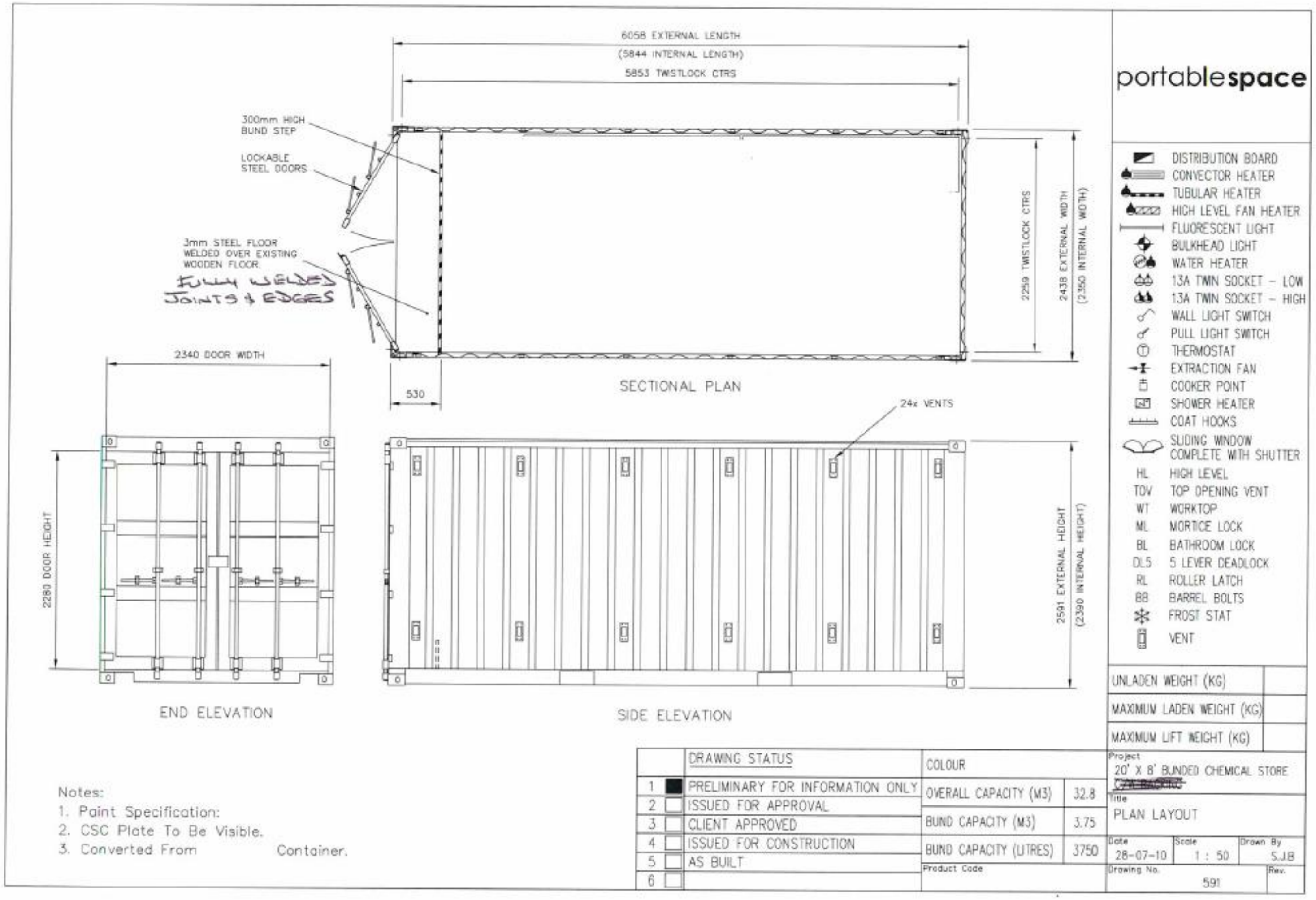


Figure 5.8: Design of 20 foot bunded container for HMI Solvent Management System.

Figure 5.9: HMI Solvent Management Container.

The system permits 'on demand' pneumatic dosing of solvent with to an accuracy of 0.1 L. The pipework for transfer allocates a flow rate of 5 L/min into the vessels. There is a dedicated solvent line made from 316 grade stainless steel for each of the solvent types used in the process -MEK, THF and IPAC.

Pneumatic diaphragm pumps are controlled by a digital dosing panel and manual ball valves at the solvent dispensing points. A 10 barg compressed air ring was installed in the HMI process room to power the ATEX rated diaphragm pumps.

The specification of the pumping system is as follows:

<u>Hoverflow 2 All-plastic Bearing Flowmeter:</u>

The system accurately measures the flow of highly corrosive, aggressive and non-lubricating liquids and chemicals. This type of flowmeter is used for measuring highly corrosive solutions such as nitric, sulphuric, hydrochloric and hydrofluoric acids so is more than suitable for the transfer or organic solvents. It is ideal for both batch and continuous process operation.

In hazardous areas the flowmeter is used in conjunction with the Apollo IS 'pick-off' coil, approved to ATEX 11 1 G Ex ia IIC T5. The signal can be used in the IS area or transmitted to the safe area using the intrinsically safe P5 preamplifier and suitable barriers.

Operation

The flowmeter has two turbines connected by a central shaft. The liquid flows through both turbines, spinning the shaft whilst it hovers. The lower turbine has magnets sealed in the rim which are detected by the sensor to generate pulses. The frequency of the pulses is proportional to the desired flow rate.

Construction

All wetted parts are either PVC/PVDF for maximum chemical resistance and the seals are PTFE. The meter combines the advantages of a turbine flowmeter without the problems of bearing wear.

Calibration

The flowmeter is individually calibrated with water and is traceable to national standards. Test certificate provided showing number of pulses per litre which is used to set the instrument.

Installation

The flowmeter is installed horizontally in the pipeline. To reduce turbulence and achieve the best results from the flowmeter it is recommended that it is installed in a straight section of pipe with at least 10 pipe diameters upstream and 5 pipe diameters downstream.

Control valves are installed downstream to the flowmeter. The flowmeter must be kept full of liquid and reverse flow must be avoided at all times.

214i Batch Controller

The instrument is used in hazardous areas to automatically batch a precise quantity of liquid. It accepts pulsed frequency signals such as those generated by turbine, positive displacement or pelton wheel flowmeters.

To start a batch the run button must be pushed. It will control pumps and valves to deliver the required volume of liquid. One display shows the batch count whilst the other will show the present quantity.

The 214i requires a DC power supply and battery back up to store the settings. It can be mounted directly onto the flowmeter, wall or pipe. The two transistor outputs are used as control valves and pumps. This allows for one or two stage batching with slow start up and/or slow shutdown of the batching process. The first output will energise at the start of the batch and de-energise when the batch is complete. The second output can be set to energise at a fixed time after the start, and to de-energise at a fixed quantity before the end of the batch.

Intrinsically Safe Installation

The 214i is certified for use in Class 1 Zone 1 hazardous areas with approved sensors and solenoids.

Construction

The instrument is housed in a polycarbonate enclosure that is weatherproof. Cables are inserted through waterproof cable glands.

Pump Specification

3 no. ½” Acetal Diaphragm Pumps.
Fitted with PTFE balls, diaphragms and seats.
According to our compatibility charts these materials are suitable for Isopropyl acetate but will need confirming.

Pipework Specification

3/8 316 Stainless steel swage lock fitted with isolators, flow valves and colour coded.

Fire Suppression:

In the event of a fire, a high-tech fire suppression system is required to distinguish the blaze as close to immediately as possible. A gas suppression (FM200) was selected rather than a classic CO_2 system. CO_2 removes 1/3rd of the fire triangle and thereby extinguishes the flame, however FM200 reacts as a chemical suppressant to inhibit the spread of fire. The system needed to comply with the ATEX regulations and ensure that room integrity was at the desired level following installation to ensure the suppression gas could not escape the environment in which it needs to be effective.

The calculations behind the fire suppression design were as follows.

Design Standards and Compliance adhered to:

Fire Detection

i. BS 5839-1:2002+A2:2008:- Fire detection & fire alarm systems for buildings. Code of practice for the design, installation, commissioning and maintenance.
ii. BS 6266:2002 Code of practice for fire protection for electronic equipment installations
iii. BS 7273-1:2006 Code of practice for the operation of fire protection measures. Electrical actuation of gaseous total flooding extinguishing systems
iv. BS EN 54 Pt1- 21 series for equipment.

Fire Suppression

i. BS EN 15004-1:2008 Fixed firefighting systems. Gas extinguishing systems. Design, installation and maintenance.

HFC-227ea (FM200) extinguishant - The current BS EN / ISO standard requires a minimum design concentration of 9% for Class 'B' (nHeptane) fires

Calculations to determine the quantity of extinguishing agent are based upon the under-mentioned dimensions and result in the risk volume shown.

Table 5.2: Risk Volume Calculation

Risk	**O/A Length**	**O/A Width**	**Room Height**	**Ceiling Void Depth**	**Floor Void Depth**	**Calculated Volume**
HMI Area	15.7m	5.9m	5.5m	N/A	N/A	509.46 m^3

Table 5.3: Mechanical System Schedule.

HFC-227ea Room Void	**Mixer Area**
HFC-227ea Extinguishant	**367.0kg**
Cylinder c/w rack and straps	**5 x 80 L**
Solenoid Master valve operator	**1**
Slave Pneumatic valve operated	**1**
180^0 Nozzle	**5**
Discharge pressure switch c/w pilot hose and adaptor	**1**
Entry warning sign	**1**
Manual discharge sign	**1**

The protected enclosure shall be bounded by rigid elements of building construction having a fire resistance of not less than 30 minutes. It is recommended that the hazard should not be closer than 0.5m from the ceiling to allow adequate distribution of extinguishant.

All total flooding systems should have the enclosure examined and tested to locate and then effectively seal any significant air leaks that could result in a failure of the protected space to hold the specified extinguishant concentration level for the appropriate duration. The preferred method is specified in Annex E of *BS EN 15004-1 / ISO 14520-1*.

An integrity test must be completed to comply with BS EN 15004/ ISO 14520. This would determine the capability of the room to contain the discharged gas at the correct concentration, and for the required time as recommended by British Standards

A means of mechanically or naturally ventilating areas after discharge of the extinguishant should be provided, with a minimum of 4 air changes per hour (HMI extraction system provides 12 air changes per hour).

It should be ensured that the post fire atmosphere is not ventilated into other areas of the building provision should be made for the prompt discovery and rescue of persons incapacitated in protected enclosures by trained persons.

The means provided for this ventilation should not form part of the normal building ventilation system and should incorporate extraction arrangements at low level in the protected area, the positioning of which is dependent on the type of extinguishant used.

The atmosphere within the risk area and adjoining areas into which the extinguishing agent may have dispersed, should be tested by a responsible person to ascertain that the atmosphere is safe for entry without breathing apparatus. No one should re-enter the area of a discharge until it is confirmed as safe to do so.

The detection system comprises of extinguishing control panel per area, isolation switch fuse, with flame detection (UV/Dual IR), bells, electronic sounder/beacons, relay (to be wired by others), remote indicators. The equipment installed as part of the HMI fire system must be intrinsically safe/ATEX rated.

Flame Detection UV/ Dual IR

The principal of the system operation is that one of the flame detectors in the risk area sensing a fire condition (first stage alarm) an alarm sounder/beacon will operate and the control panel will indicate the alarm indication. This indicates that there is a problem in the risk area and initiation of gas release will begin (Time delay of 30 seconds programmed in).

Control panel

The control panel is manufactured in accordance with BS EN54 BS EN 54 Pt1- 21 series for equipment. The control panel also incorporates a manual release facility together with an auto/manual key switch.

The status is indicated by:

System Isolated - Twin Amber LEDs
Automatic/Manual - Twin Amber LEDs
Manual Only - Twin Green LEDs
Discharged - Twin Red LEDs

Extraction System:

The aforementioned extraction system designed to remove the VOC vapour produced during manufacturing to ensure compliance to workplace exposure limits has the following design specification. See the design drawing in figure 5.10.

Air Input:

- Air changes of 10 to 12 cycles per hour utilising the existing system previously installed for the material warehouse.
- The positive air was ducted through a 900 to 300 mm reducing cowl with inline off driven spring return damper (this being the airflow closure on fire alarm activation). A second internal fire damper in the 300mm incoming ducting has been afforded to terminate any fire path.
- On entry into the works area six adjustable dampers were fitted to each input point.
- Input ducting was suspended at room entry height as per external air manifold.

Work Area Extract:

- Floor level 250mm ducting with discharge grills was installed.
- Ducting was constructed and terminated at roof top outcrop *via* an ATEX bifurcating fan and euro cowl output.

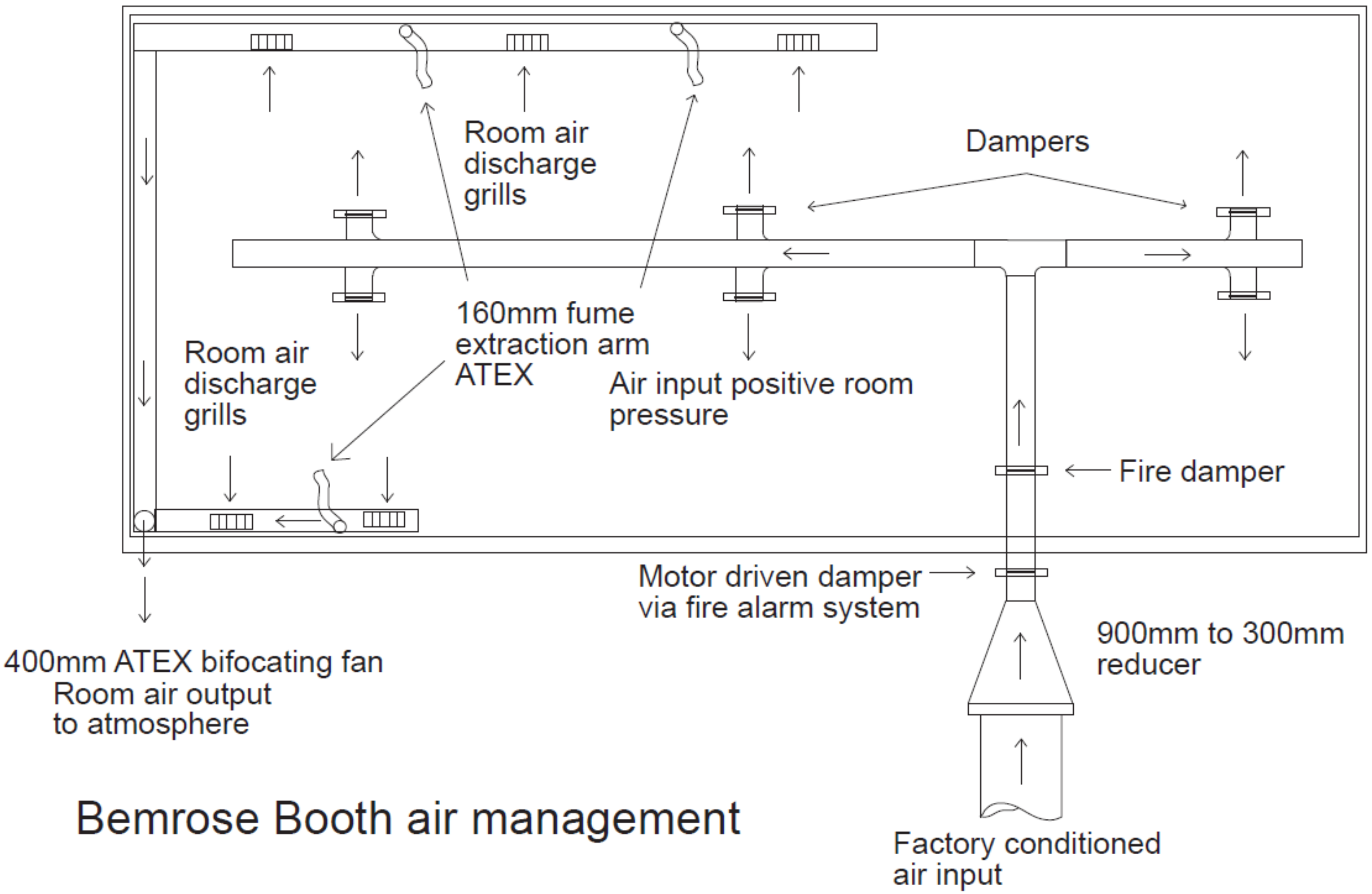


Figure 5.10: Extraction system design for HMI.

The completed facility (to original design capacity) can be seen in figures 5.11 to 5.16.

5.11: 30s and 60s Attritors.

5.12: Solvent pumping system and solvent barrel.

5.13: HL0104 finished product prepared for shipment to Argent.

5.14: R&D laboratory with pilot scale mini attritor.

5.15: HMI Quality Control laboratory.

5.16: Analytical equipment in HMI QC laboratory.

5.2 HMI SHE

In order to carry out the required due diligence in developing the process, it was hugely important to understand the potential impact of the process hazards. The following section demonstrates the worst-case consequence modelling studies completed on the solvent quantities handled in the HMI process.

Boiling Liquid Expanding Vapour Explosion - Large Resin Mixer:

HMI Large Resin Mixer:

Latitude = 53.773561°N, Longitude = 0.335182°W

Still Conditions for a boiling liquid expanding vapour explosion.

Could occur with heat build-up and ignition source, i.e. no cooling to system.

Figure 5.17 depicts a blast radius for a BLEVE of the large resin mixer in HMI, using Aloha software.

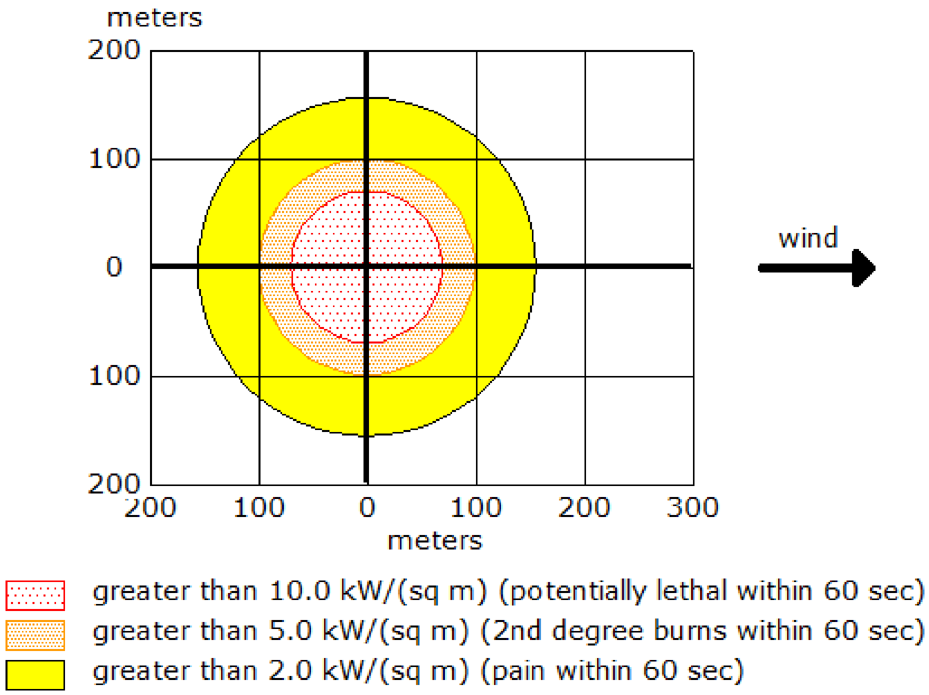


Figure 5.17: Blast radius of Large Resin Mixer (including potential effects).

Using Marplot software, the direct geographical effect of this explosion is captured (figure 5.18).

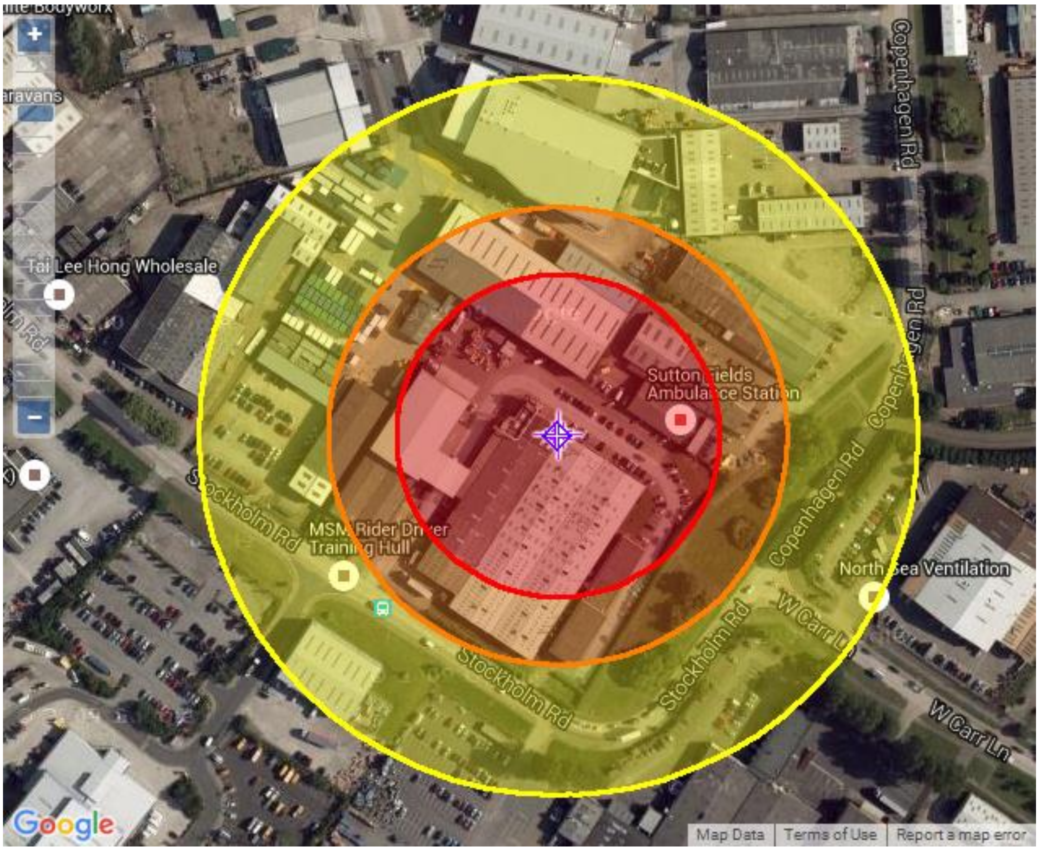


Figure 5.18: Plotting of HMI Large Resin Mixer BLEVE using Marplot.

<u>BLEVE Full Solvent Inventory:</u>

HMI Full Solvent Inventory including full process:

Latitude = 53.773561°N, Longitude = 0.335182°W

Still conditions for a boiling liquid expanding vapour explosion.

Could occur with heat build-up and ignition source, *i.e.* no cooling to system.

Figure 5.19 depicts a blast wave representative of the full solvent inventory of HMI including that within the process, and the resulting consequences.

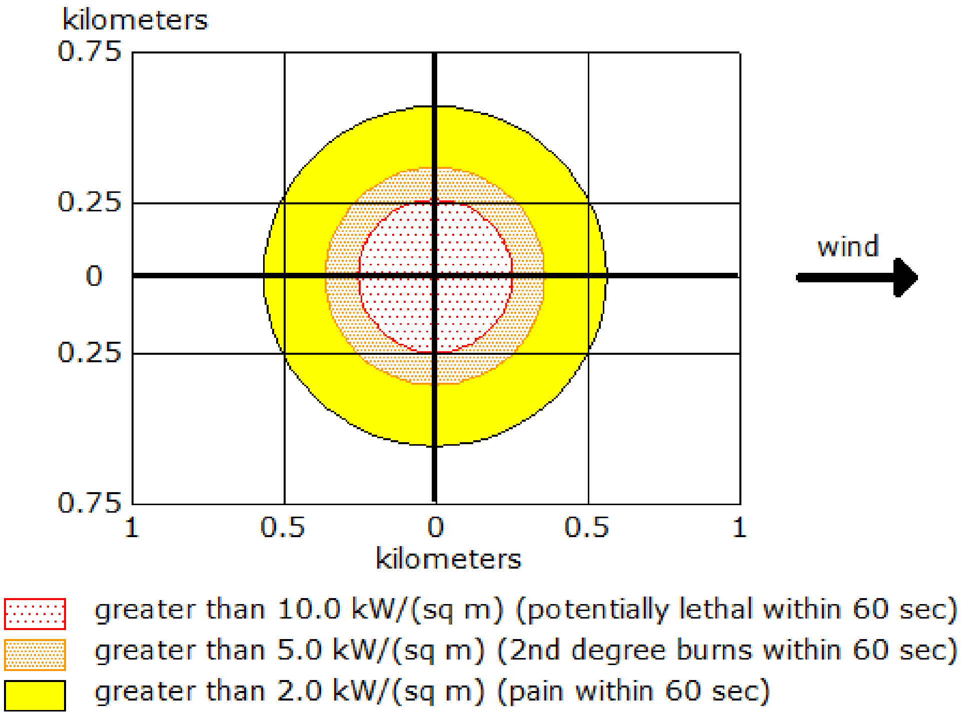


Figure 5.19: Blast radius of HMI full solvent inventory (including potential effects).

As for the large resin mixer, the direct geographical effect of this explosion is captured in figure 5.20.

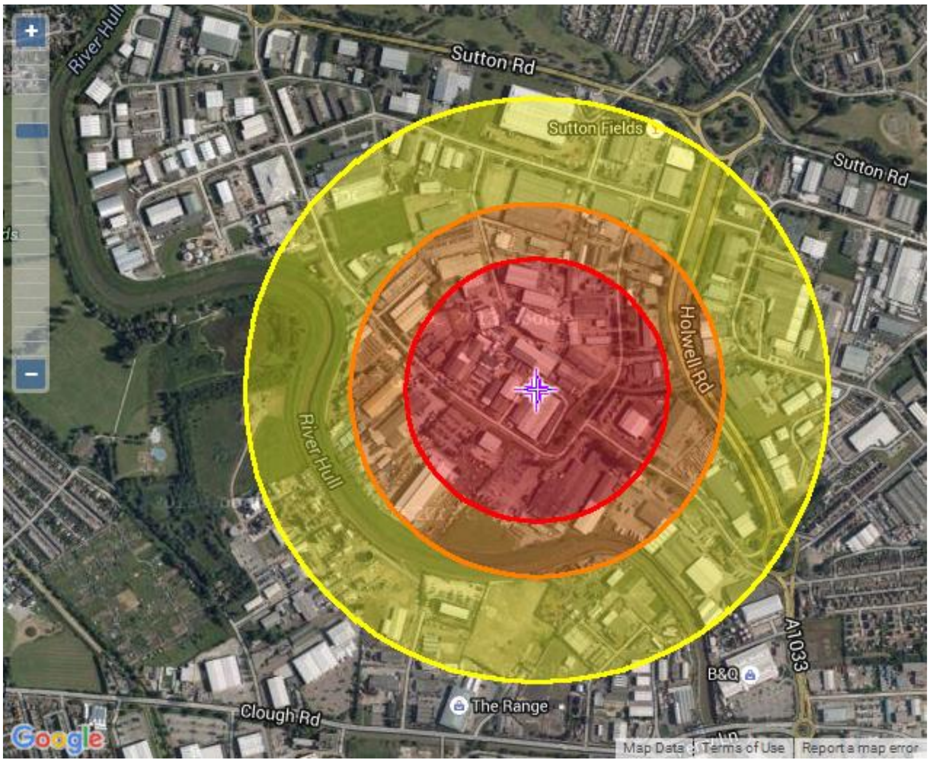
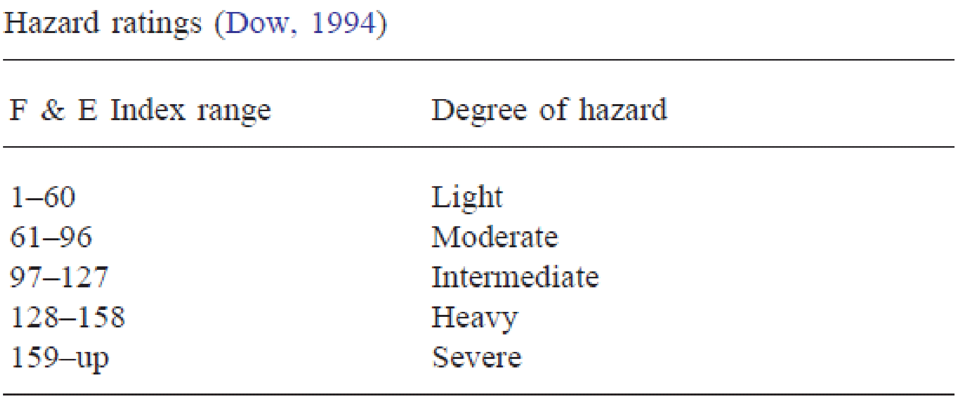


Figure 5.20: Plotting of HMI full solvent inventory BLEVE using Marplot.

In the event that the processing volumes or conditions increase, the site has potential to break into the lower tier COMAH regulations. A Major Accident Prevention Policy has been drafted for this eventuality and is available in Appendix 3:

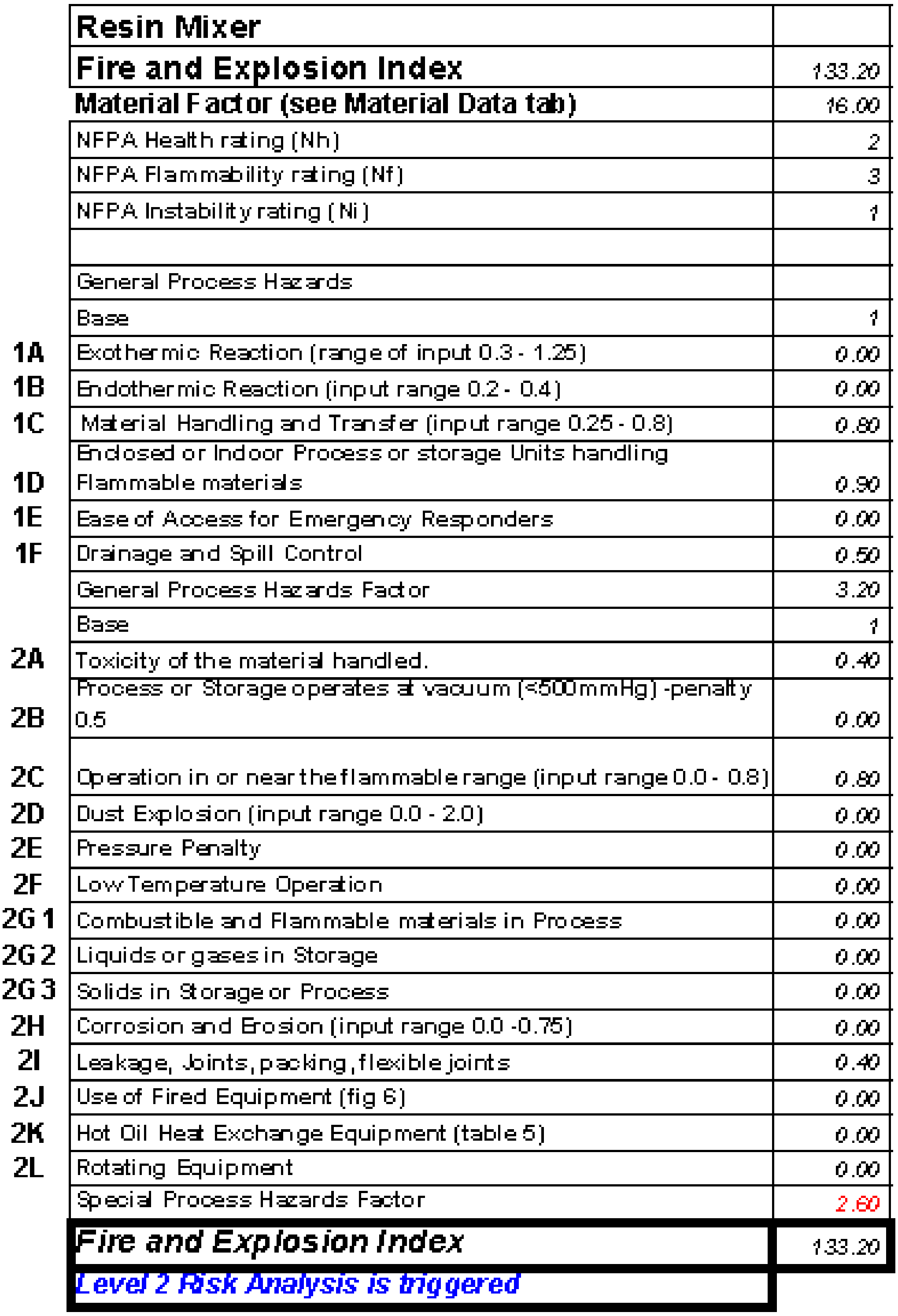
A DOW Fire and Explosion Index has been executed to understand the status of the manufacturing facility when using the most hazardous piece of process equipment, the large resin mixer. At a score of 1.33 (see Table 5.4 and figure 5.21 below), the conclusion is that there is a heavy hazard during start-up, and that extra precautions must be taken in material handling to mitigate this risk.

Table 5.4: DOW F&EI Hazard Ratings.



Hazard ratings (Dow, 1994)

F & E Index range	Degree of hazard
1–60	Light
61–96	Moderate
97–127	Intermediate
128–158	Heavy
159–up	Severe

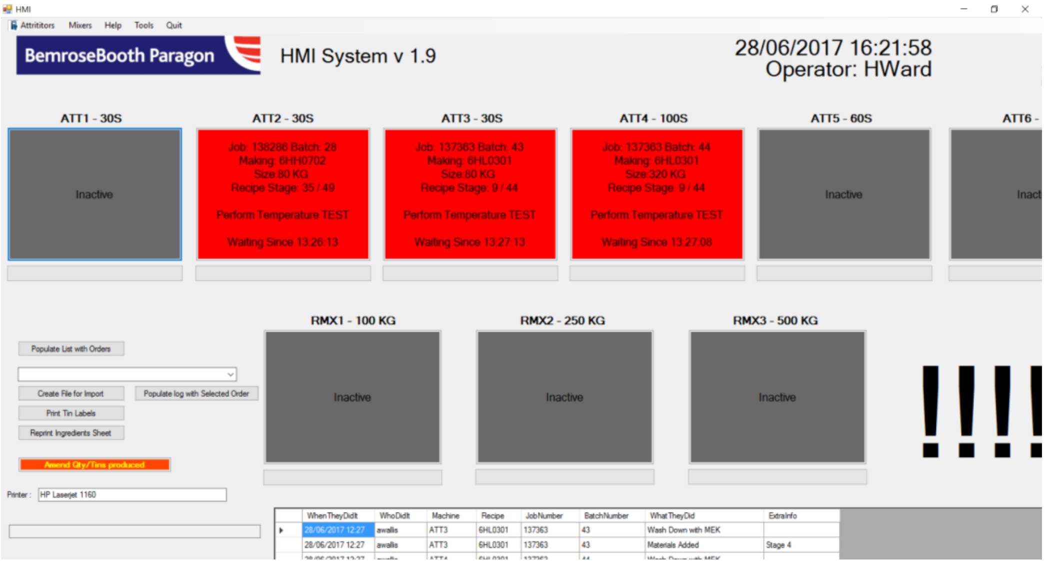


	Resin Mixer	
	Fire and Explosion Index	133.20
	Material Factor (see Material Data tab)	16.00
	NFPA Health rating (Nh)	2
	NFPA Flammability rating (Nf)	3
	NFPA Instability rating (Ni)	1
	General Process Hazards	
	Base	1
1A	Exothermic Reaction (range of input 0.3 - 1.25)	0.00
1B	Endothermic Reaction (input range 0.2 - 0.4)	0.00
1C	Material Handling and Transfer (input range 0.25 - 0.8)	0.80
1D	Enclosed or Indoor Process or storage Units handling Flammable materials	0.90
1E	Ease of Access for Emergency Responders	0.00
1F	Drainage and Spill Control	0.50
	General Process Hazards Factor	3.20
	Base	1
2A	Toxicity of the material handled.	0.40
2B	Process or Storage operates at vacuum (<500mmHg) -penalty 0.5	0.00
2C	Operation in or near the flammable range (input range 0.0 - 0.8)	0.80
2D	Dust Explosion (input range 0.0 - 2.0)	0.00
2E	Pressure Penalty	0.00
2F	Low Temperature Operation	0.00
2G 1	Combustible and Flammable materials in Process	0.00
2G 2	Liquids or gases in Storage	0.00
2G 3	Solids in Storage or Process	0.00
2H	Corrosion and Erosion (input range 0.0 -0.75)	0.00
2I	Leakage, Joints, packing, flexible joints	0.40
2J	Use of Fired Equipment (fig 6)	0.00
2K	Hot Oil Heat Exchange Equipment (table 5)	0.00
2L	Rotating Equipment	0.00
	Special Process Hazards Factor	2.60
	Fire and Explosion Index	133.20
	Level 2 Risk Analysis is triggered	

Figure 5.21: DOW F&EI result for HMI

A What-if analysis was completed to identify and reduce risks in the process. A HAZOP was deemed too complex for the process. The results of this What-If are presented in Appendix 4.

Although much of the process is manual, process control parameters have been implemented where possible. A bespoke piece of software called the 'HMI System' was created to manage the activities of each machine. It facilitates the operators role through providing step-by-step instruction for every chemical manufacturing stage. Each box represents a piece of process machinery and if red, and action is required. The operator must click on the red box, and is instructed on the following required action. A screenshot of the process is available in figure 5.22.



28/06/2017 16:21:58
Operator: HWard

ATT2 - 30S: Job: 138286 Batch: 28
Making: 6HH0702
Size:80 KG
Recipe Stage: 35 / 49
Perform Temperature TEST
Waiting Since 13:26:13

ATT3 - 30S: Job: 137363 Batch: 43
Making: 6HL0301
Size:80 KG
Recipe Stage: 9 / 44
Perform Temperature TEST
Waiting Since 13:27:13

ATT4 - 100S: Job: 137363 Batch: 44
Making: 6HL0301
Size:320 KG
Recipe Stage: 9 / 44
Perform Temperature TEST
Waiting Since 13:27:08

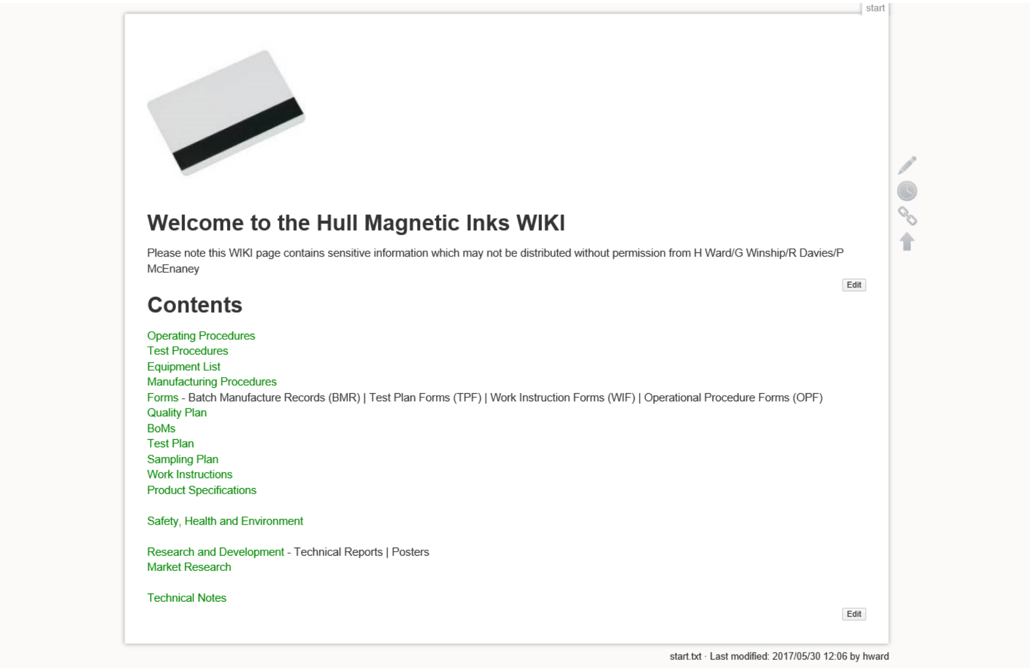
Printer : HP Laserjet 1160

WhenTheyDidIt	WhoDidIt	Machine	Recipe	JobNumber	BatchNumber	WhatTheyDid	ExtraInfo
28/06/2017 12:27	awallis	ATT3	6HL0301	137363	43	Wash Down with MEK	
28/06/2017 12:27	awallis	ATT3	6HL0301	137363	43	Materials Added	Stage 4

Figure 5.22: Screenshot of the HMI Software.

5.4 Implementation and Maintenance

In order to log the processing instructions, SHE, R&D and maintain guarded access on formulations, a centralized database dedicated to HMI was created. The database is limited access only and contains over 200 documents written to regulate the process. The documents include operating procedures, test procedures, quality plans, test plans *etc.* A screenshot of the home page is displayed in figure 5.23 and an example of an operating procedure and MSDS are in Appendix 5 and 6 respectively.



Welcome to the Hull Magnetic Inks WIKI

Please note this WIKI page contains sensitive information which may not be distributed without permission from H Ward/G Winship/R Davies/P McEnaney

Contents

Operating Procedures
Test Procedures
Equipment List
Manufacturing Procedures
Forms - Batch Manufacture Records (BMR) | Test Plan Forms (TPF) | Work Instruction Forms (WIF) | Operational Procedure Forms (OPF)
Quality Plan
BoMs
Test Plan
Sampling Plan
Work Instructions
Product Specifications

Safety, Health and Environment

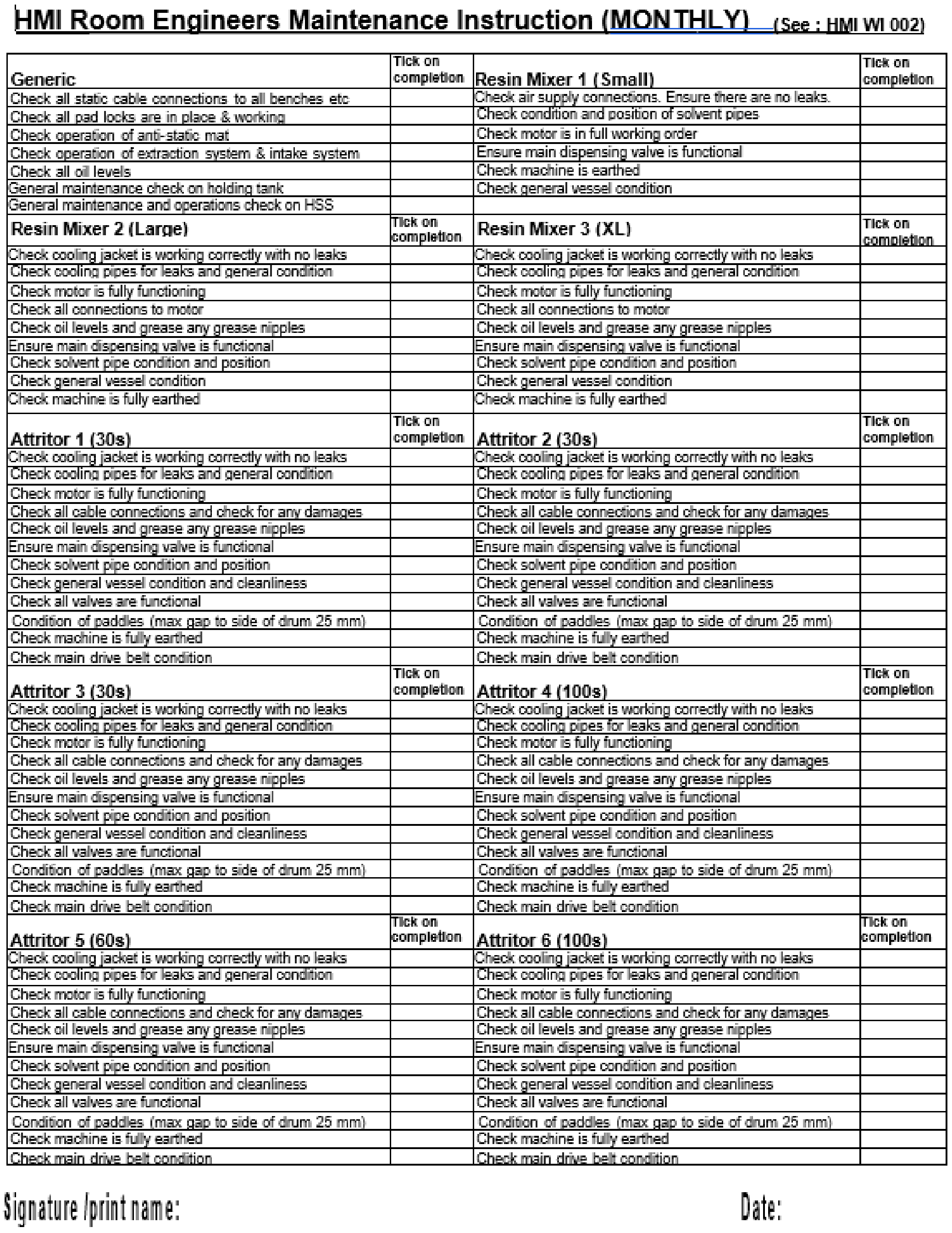
Research and Development - Technical Reports | Posters
Market Research

Technical Notes

start.txt · Last modified: 2017/05/30 12:06 by hward

Figure 5.23: Screenshot of HMI Wiki Homepage.

A strict maintenance schedule has been devised for the HMI Process Room, particularly as an outcome of the What-If study completed on process safety. It can be seen in figure 5.24 below.



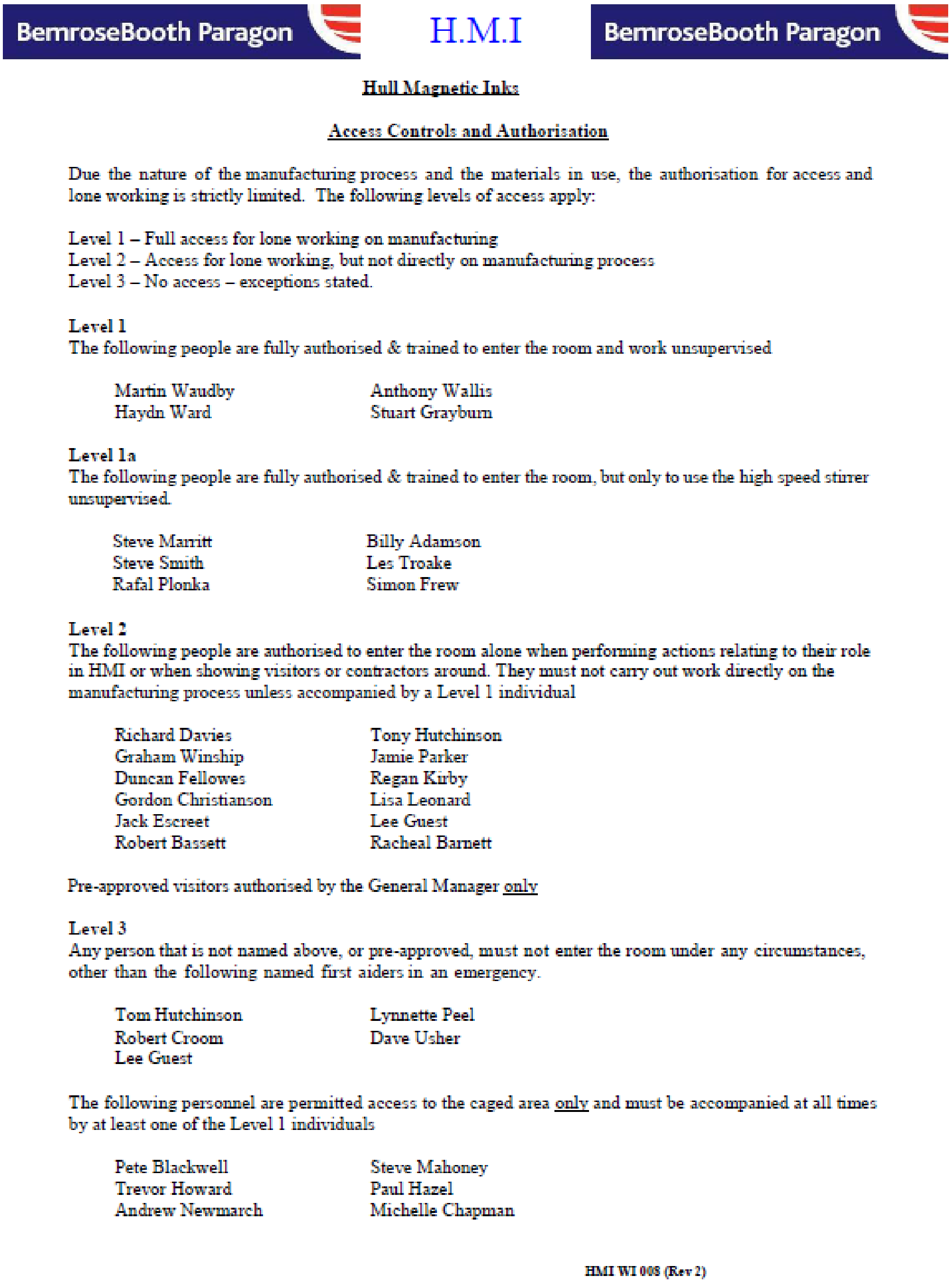
HMI Room Engineers Maintenance Instruction (MONTHLY) (See : HMI WI 002)

Generic	Tick on completion	**Resin Mixer 1 (Small)**	Tick on completion
Check all static cable connections to all benches etc		Check air supply connections. Ensure there are no leaks.	
Check all pad locks are in place & working		Check condition and position of solvent pipes	
Check operation of anti-static mat		Check motor is in full working order	
Check operation of extraction system & intake system		Ensure main dispensing valve is functional	
Check all oil levels		Check machine is earthed	
General maintenance check on holding tank		Check general vessel condition	
General maintenance and operations check on HSS			
Resin Mixer 2 (Large)	Tick on completion	**Resin Mixer 3 (XL)**	Tick on completion
Check cooling jacket is working correctly with no leaks		Check cooling jacket is working correctly with no leaks	
Check cooling pipes for leaks and general condition		Check cooling pipes for leaks and general condition	
Check motor is fully functioning		Check motor is fully functioning	
Check all connections to motor		Check all connections to motor	
Check oil levels and grease any grease nipples		Check oil levels and grease any grease nipples	
Ensure main dispensing valve is functional		Ensure main dispensing valve is functional	
Check solvent pipe condition and position		Check solvent pipe condition and position	
Check general vessel condition		Check general vessel condition	
Check machine is fully earthed		Check machine is fully earthed	
Attritor 1 (30s)	Tick on completion	**Attritor 2 (30s)**	Tick on completion
Check cooling jacket is working correctly with no leaks		Check cooling jacket is working correctly with no leaks	
Check cooling pipes for leaks and general condition		Check cooling pipes for leaks and general condition	
Check motor is fully functioning		Check motor is fully functioning	
Check all cable connections and check for any damages		Check all cable connections and check for any damages	
Check oil levels and grease any grease nipples		Check oil levels and grease any grease nipples	
Ensure main dispensing valve is functional		Ensure main dispensing valve is functional	
Check solvent pipe condition and position		Check solvent pipe condition and position	
Check general vessel condition and cleanliness		Check general vessel condition and cleanliness	
Check all valves are functional		Check all valves are functional	
Condition of paddles (max gap to side of drum 25 mm)		Condition of paddles (max gap to side of drum 25 mm)	
Check machine is fully earthed		Check machine is fully earthed	
Check main drive belt condition		Check main drive belt condition	
Attritor 3 (30s)	Tick on completion	**Attritor 4 (100s)**	Tick on completion
Check cooling jacket is working correctly with no leaks		Check cooling jacket is working correctly with no leaks	
Check cooling pipes for leaks and general condition		Check cooling pipes for leaks and general condition	
Check motor is fully functioning		Check motor is fully functioning	
Check all cable connections and check for any damages		Check all cable connections and check for any damages	
Check oil levels and grease any grease nipples		Check oil levels and grease any grease nipples	
Ensure main dispensing valve is functional		Ensure main dispensing valve is functional	
Check solvent pipe condition and position		Check solvent pipe condition and position	
Check general vessel condition and cleanliness		Check general vessel condition and cleanliness	
Check all valves are functional		Check all valves are functional	
Condition of paddles (max gap to side of drum 25 mm)		Condition of paddles (max gap to side of drum 25 mm)	
Check machine is fully earthed		Check machine is fully earthed	
Check main drive belt condition		Check main drive belt condition	
Attritor 5 (60s)	Tick on completion	**Attritor 6 (100s)**	Tick on completion
Check cooling jacket is working correctly with no leaks		Check cooling jacket is working correctly with no leaks	
Check cooling pipes for leaks and general condition		Check cooling pipes for leaks and general condition	
Check motor is fully functioning		Check motor is fully functioning	
Check all cable connections and check for any damages		Check all cable connections and check for any damages	
Check oil levels and grease any grease nipples		Check oil levels and grease any grease nipples	
Ensure main dispensing valve is functional		Ensure main dispensing valve is functional	
Check solvent pipe condition and position		Check solvent pipe condition and position	
Check general vessel condition and cleanliness		Check general vessel condition and cleanliness	
Check all valves are functional		Check all valves are functional	
Condition of paddles (max gap to side of drum 25 mm)		Condition of paddles (max gap to side of drum 25 mm)	
Check machine is fully earthed		Check machine is fully earthed	
Check main drive belt condition		Check main drive belt condition	

Signature /print name: **Date:**

Figure 5.24: HMI Engineering Monthly Maintenance Schedule.

The following document states the defined access levels to the code-locked process room. Only authorized Level 1 personnel may enter/work alone.



BemroseBooth Paragon H.M.I BemroseBooth Paragon

Hull Magnetic Inks

Access Controls and Authorisation

Due the nature of the manufacturing process and the materials in use, the authorisation for access and lone working is strictly limited. The following levels of access apply:

Level 1 – Full access for lone working on manufacturing
Level 2 – Access for lone working, but not directly on manufacturing process
Level 3 – No access – exceptions stated.

Level 1
The following people are fully authorised & trained to enter the room and work unsupervised

Martin Waudby
Haydn Ward
Anthony Wallis
Stuart Grayburn

Level 1a
The following people are fully authorised & trained to enter the room, but only to use the high speed stirrer unsupervised.

Steve Marritt
Steve Smith
Rafal Plonka
Billy Adamson
Les Troake
Simon Frew

Level 2
The following people are authorised to enter the room alone when performing actions relating to their role in HMI or when showing visitors or contractors around. They must not carry out work directly on the manufacturing process unless accompanied by a Level 1 individual

Richard Davies
Graham Winship
Duncan Fellowes
Gordon Christianson
Jack Escreet
Robert Bassett
Tony Hutchinson
Jamie Parker
Regan Kirby
Lisa Leonard
Lee Guest
Racheal Barnett

Pre-approved visitors authorised by the General Manager <u>only</u>

Level 3
Any person that is not named above, or pre-approved, must not enter the room under any circumstances, other than the following named first aiders in an emergency.

Tom Hutchinson
Robert Croom
Lee Guest
Lynnette Peel
Dave Usher

The following personnel are permitted access to the caged area <u>only</u> and must be accompanied at all times by at least one of the Level 1 individuals

Pete Blackwell
Trevor Howard
Andrew Newmarch
Steve Mahoney
Paul Hazel
Michelle Chapman

HMI WI 008 (Rev 2)

Figure 5.25: Personnel Access Control.

Access level to the facility is determined by the level of training the individual has received. Level 1 operators are trained three times on each task before being considered competent without supervision and this has been recorded in a training matrix/training manual. Each operator has also been subjected to a specifically targeted Chemical Handling Training session.

5.5 QA/QC of Manufactured Product

To ensure that the manufactured product in the HMI facility is maintained to the exacting standards within which it was developed, continual monitoring of batch results takes place and is back-logged in a database by the HMI software. See Table 5.5 below for an example of the data tracking which has taken place over the month of April for HL0104.

Table 5.5: Data logging for HL0104 in April 2016.

Visc (cP)	Hm	Hc (Oe)	Sat	Rem	Sq	SFD	Att Size	Att Name	Mfg date	Exp date
1840	1500	326	1650	1170	0.712	0.575	60	1	07-Apr-15	06-Apr-16
1700	1470	334	1580	1130	0.716	0.57	60	1	22-Apr-15	21-Apr-16
1220	1500	338	1550	1140	0.739	0.592	30	5	22-Apr-15	21-Apr-16
1440	1470	338	1490	1050	0.71	0.581	30	2	22-Apr-15	21-Apr-16
2500	1500	333	1890	1410	0.746	0.565	60	1	23-Apr-15	22-Apr-16
1460	1510	337	1990	1460	0.733	0.588	30	5	23-Apr-15	22-Apr-16
1600	1470	338	1810	1320	0.73	0.556	30	2	23-Apr-15	22-Apr-16
1900	1470	335	1610	1160	0.719	0.626	60	1	24-Apr-15	23-Apr-16
1380	1490	339	1670	1240	0.741	0.601	30	5	24-Apr-15	23-Apr-16
1640	1460	339	1580	1130	0.714	0.566	30	2	24-Apr-15	23-Apr-16
2320	1470	338	1740	1300	0.746	0.589	60	1	27-Apr-15	26-Apr-16
1200	1480	337	1330	964	0.725	0.665	30	5	27-Apr-15	26-Apr-16
1560	1500	337	1630	1220	0.747	0.523	30	2	27-Apr-15	26-Apr-16
2280	1480	336	1860	1390	0.745	0.545	60	1	28-Apr-15	27-Apr-16
1760	1480	334	1750	1320	0.753	0.583	30	5	28-Apr-15	27-Apr-16
1680	1490	334	1700	1280	0.751	0.6	30	2	28-Apr-15	27-Apr-16
2720	1480	335	1490	1130	0.759	0.561	60	1	29-Apr-15	28-Apr-16
2000	1490	330	1740	1270	0.731	0.545	30	5	29-Apr-15	28-Apr-16
1860	1480	338	1520	1170	0.773	0.515	30	2	29-Apr-15	28-Apr-16
2280	1470	332	1780	1340	0.752	0.535	60	1	30-Apr-15	29-Apr-16
1920	1460	330	1630	1190	0.728	0.625	30	5	30-Apr-15	29-Apr-16
2180	1500	339	1540	1270	0.82	0.632	30	2	30-Apr-15	29-Apr-16
2100	1470	334	1530	1160	0.758	0.547	60	1	01-May-15	30-Apr-16
1600	1510	333	1500	1130	0.753	0.587	30	5	01-May-15	30-Apr-16
2040	1500	334	1470	1130	0.767	0.564	30	2	01-May-15	30-Apr-16
1840	1500	331	1640	1190	0.723	0.554	30	5	01-May-15	30-Apr-16

These data are stored and represented to the operators in the form of a Shewhart chart as below in figure 5.26.

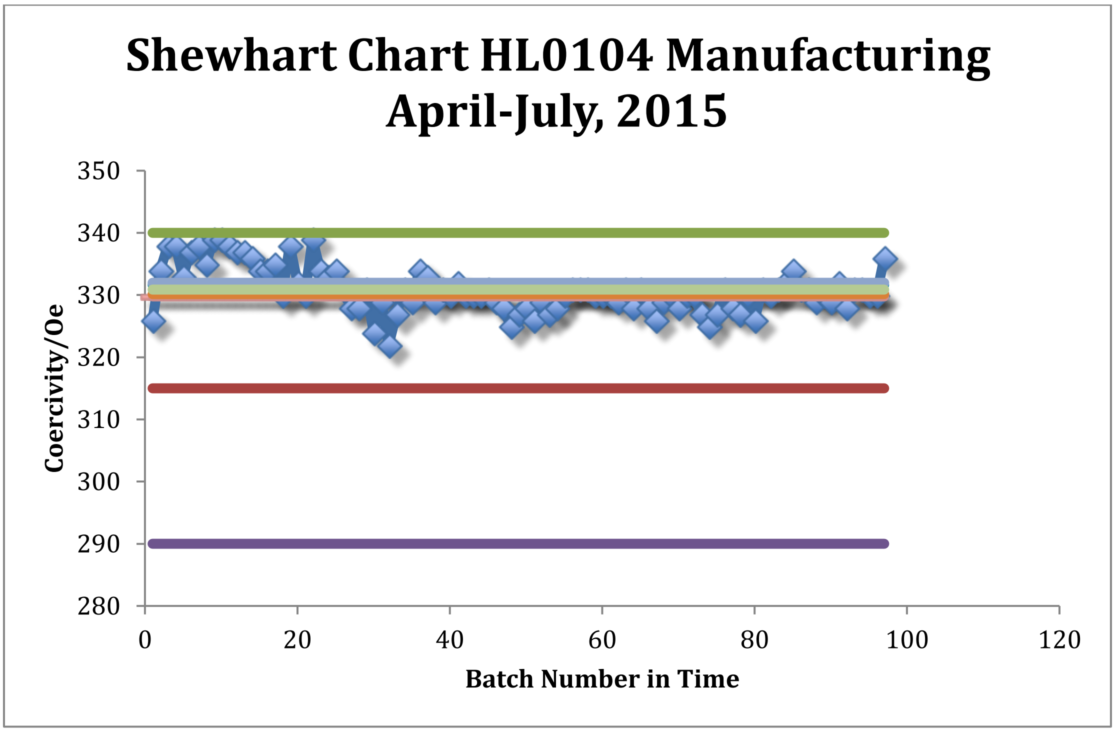


Figure 5.26: Shewhart Chart showing typical monitoring of HMI products.

In the next chapter, the economics of ink manufacture are considered.

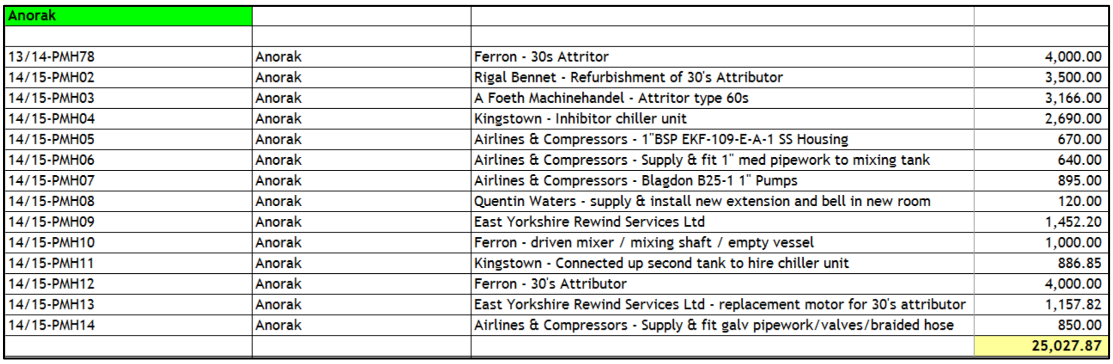
Chapter 6 – Economics of Ink Manufacture

This chapter assesses both the budget *vs*. actual for the project, showing the BBP HMI asset register, and the ongoing economics of ink manufacture following the completion of the facility.

The project budget was set at £150k for installation of the process room and three attritor machines plus two resin mixers.

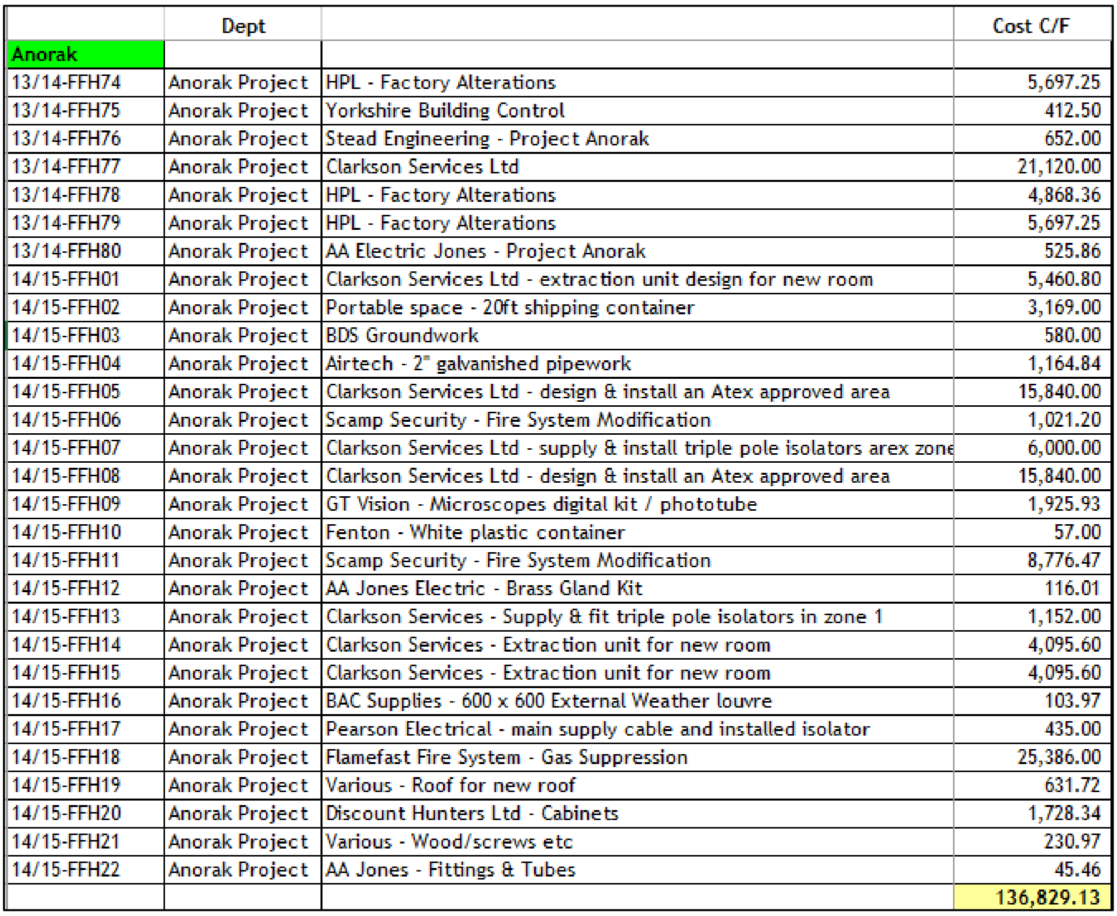
The asset register for HMI for the items under this original budget is split into tables 6.1 and 6.2 below, the first is Plant and Machinery, the second is Fixtures and Fittings.

Table 6.1: Plant and Machinery register (units in £)



Anorak			
13/14-PMH78	Anorak	Ferron - 30s Attritor	4,000.00
14/15-PMH02	Anorak	Rigal Bennet - Refurbishment of 30's Attributor	3,500.00
14/15-PMH03	Anorak	A Foeth Machinehandel - Attritor type 60s	3,166.00
14/15-PMH04	Anorak	Kingstown - Inhibitor chiller unit	2,690.00
14/15-PMH05	Anorak	Airlines & Compressors - 1"BSP EKF-109-E-A-1 SS Housing	670.00
14/15-PMH06	Anorak	Airlines & Compressors - Supply & fit 1" med pipework to mixing tank	640.00
14/15-PMH07	Anorak	Airlines & Compressors - Blagdon B25-1 1" Pumps	895.00
14/15-PMH08	Anorak	Quentin Waters - supply & install new extension and bell in new room	120.00
14/15-PMH09	Anorak	East Yorkshire Rewind Services Ltd	1,452.20
14/15-PMH10	Anorak	Ferron - driven mixer / mixing shaft / empty vessel	1,000.00
14/15-PMH11	Anorak	Kingstown - Connected up second tank to hire chiller unit	886.85
14/15-PMH12	Anorak	Ferron - 30's Attributor	4,000.00
14/15-PMH13	Anorak	East Yorkshire Rewind Services Ltd - replacement motor for 30's attributor	1,157.82
14/15-PMH14	Anorak	Airlines & Compressors - Supply & fit galv pipework/valves/braided hose	850.00
			25,027.87

Table 6.2: Fixtures and Fittings Asset Register (units in £).



	Dept		Cost C/F
Anorak			
13/14-FFH74	Anorak Project	HPL - Factory Alterations	5,697.25
13/14-FFH75	Anorak Project	Yorkshire Building Control	412.50
13/14-FFH76	Anorak Project	Stead Engineering - Project Anorak	652.00
13/14-FFH77	Anorak Project	Clarkson Services Ltd	21,120.00
13/14-FFH78	Anorak Project	HPL - Factory Alterations	4,868.36
13/14-FFH79	Anorak Project	HPL - Factory Alterations	5,697.25
13/14-FFH80	Anorak Project	AA Electric Jones - Project Anorak	525.86
14/15-FFH01	Anorak Project	Clarkson Services Ltd - extraction unit design for new room	5,460.80
14/15-FFH02	Anorak Project	Portable space - 20ft shipping container	3,169.00
14/15-FFH03	Anorak Project	BDS Groundwork	580.00
14/15-FFH04	Anorak Project	Airtech - 2" galvanished pipework	1,164.84
14/15-FFH05	Anorak Project	Clarkson Services Ltd - design & install an Atex approved area	15,840.00
14/15-FFH06	Anorak Project	Scamp Security - Fire System Modification	1,021.20
14/15-FFH07	Anorak Project	Clarkson Services Ltd - supply & install triple pole isolators arex zone	6,000.00
14/15-FFH08	Anorak Project	Clarkson Services Ltd - design & install an Atex approved area	15,840.00
14/15-FFH09	Anorak Project	GT Vision - Microscopes digital kit / phototube	1,925.93
14/15-FFH10	Anorak Project	Fenton - White plastic container	57.00
14/15-FFH11	Anorak Project	Scamp Security - Fire System Modification	8,776.47
14/15-FFH12	Anorak Project	AA Jones Electric - Brass Gland Kit	116.01
14/15-FFH13	Anorak Project	Clarkson Services - Supply & fit triple pole isolators in zone 1	1,152.00
14/15-FFH14	Anorak Project	Clarkson Services - Extraction unit for new room	4,095.60
14/15-FFH15	Anorak Project	Clarkson Services - Extraction unit for new room	4,095.60
14/15-FFH16	Anorak Project	BAC Supplies - 600 x 600 External Weather louvre	103.97
14/15-FFH17	Anorak Project	Pearson Electrical - main supply cable and installed isolator	435.00
14/15-FFH18	Anorak Project	Flamefast Fire System - Gas Suppression	25,386.00
14/15-FFH19	Anorak Project	Various - Roof for new roof	631.72
14/15-FFH20	Anorak Project	Discount Hunters Ltd - Cabinets	1,728.34
14/15-FFH21	Anorak Project	Various - Wood/screws etc	230.97
14/15-FFH22	Anorak Project	AA Jones - Fittings & Tubes	45.46
			136,829.13

With regards to original budget value, the spend has been within reasonable agreement. Overspending by approximately £11,857.

It was, however, following project initiation, realized that the budget required to achieve the desired capacity to meet customer need would need to be increased. This included a further three attritors, another resin mixer and a high shear disperser along with all fixtures and fittings. The total actual spend was nearer to £350k, however the following financial calculations have been made incorporating the original budget for consistency throughout.

The flow chart in figure 6.1 demonstrates the route through which basic economic calculations on the ink products were made. The financial calculations that proceed thereafter are considered with respect to floor space on the site, and so profit margins may seem higher and material costs lower than the actual cost, moreover HMI has been considered by its proportional contribution to the turnover and profit of the site.

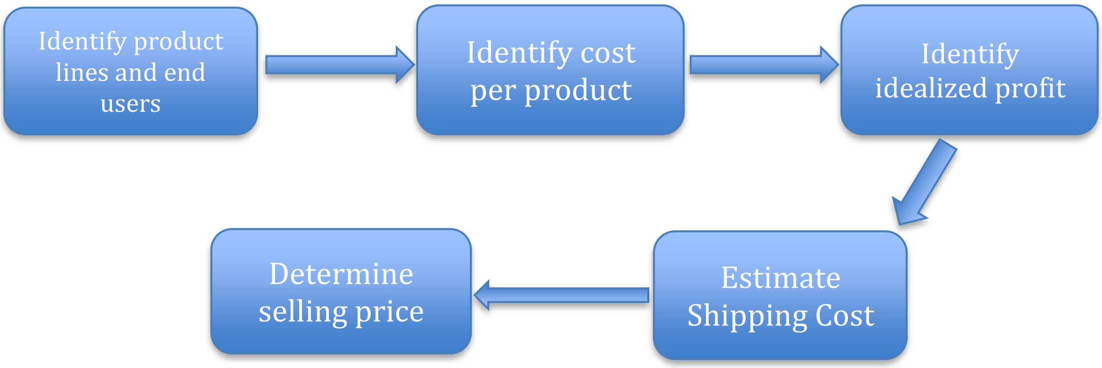


Figure 6.1: Flow diagram for determining profit on each ink product.

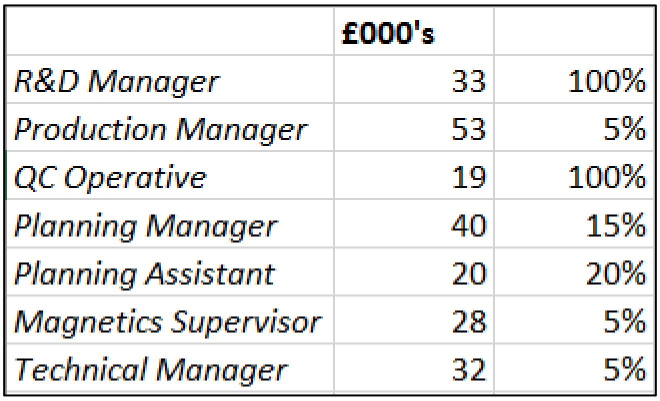
The list of customer-approved magnetic ink products and their quantities have been assembled below in Table 6.3 for analysis. Material cost has been calculated separately for each ink (example in Appendix 7), and is incorporated into the calculation for each product to understand the price per kg based on floor space.

Table 6.3: HMI approved products and annual production volumes (in kg).

Description		**Estimated Annual Production**	**Apportionment %**
HL0104 - LOCO Argent		36440	24.57%
HL0201 - LOCO Argent		12000	8.09%
HL0301 - UK Rail		77000	51.92%
HL0401 - Bank of Brazil		4000	2.70%
HL0601 - Low Output Ink		160	0.11%
HH0104 - HICO Argent		3000	2.02%
HH0401 - Hull Inhouse HICO		951	0.64%
HH0702 - Boston HICO		14760	9.95%
		148311	**100.00%**

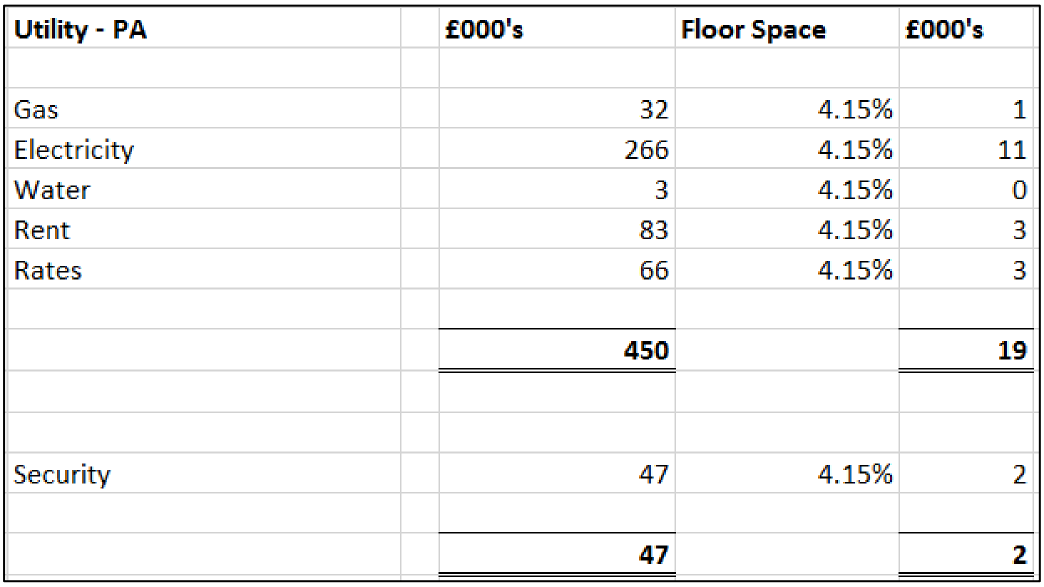
The following Tables 6.4 and 6.5 show salaries and apportionment, and utility costs apportioned by floor space.

Table 6.4: Salaries and apportionment of individuals involved in HMI



	£000's	
R&D Manager	33	100%
Production Manager	53	5%
QC Operative	19	100%
Planning Manager	40	15%
Planning Assistant	20	20%
Magnetics Supervisor	28	5%
Technical Manager	32	5%

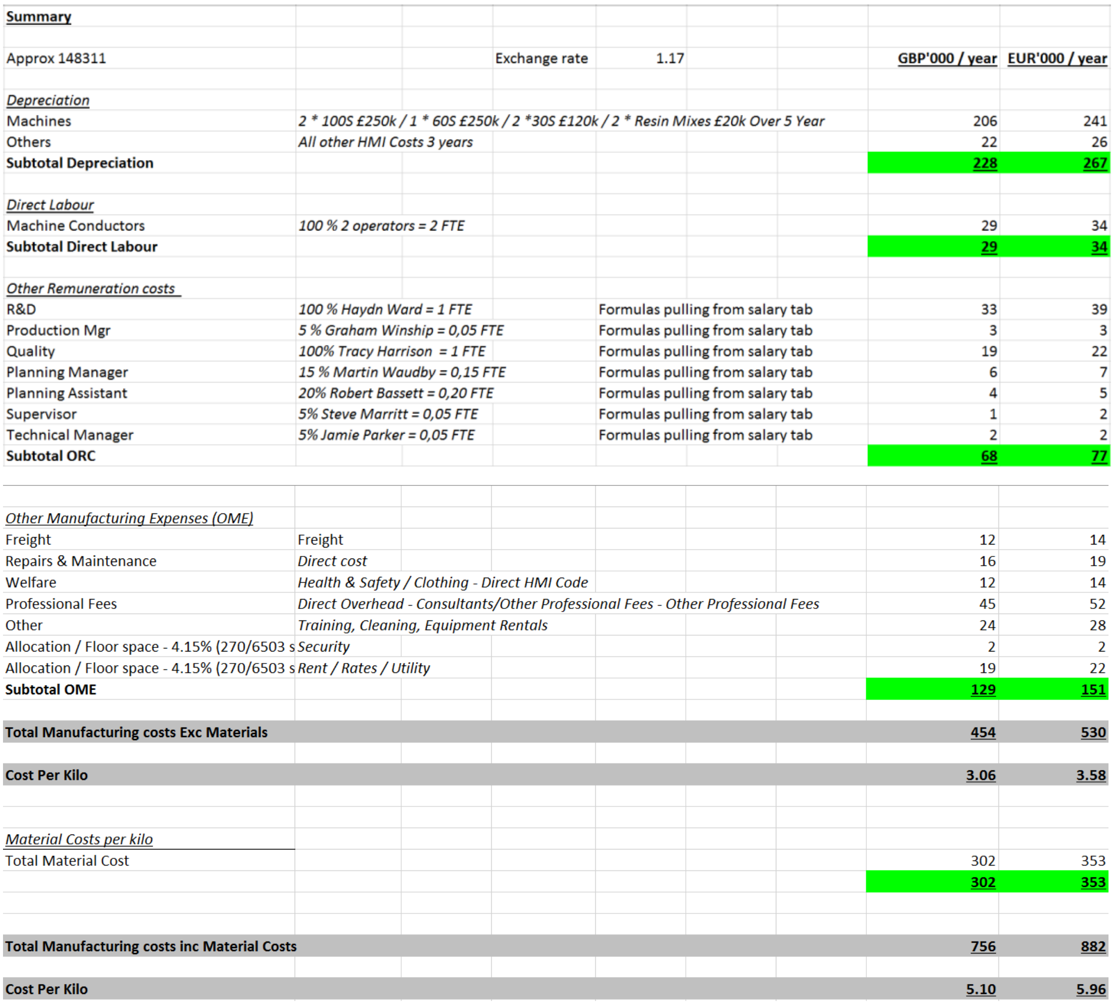
Table 6.5: Utility costs at BBP and HMI floor space apportionment



Utility - PA	**£000's**	**Floor Space**	**£000's**
Gas	32	4.15%	1
Electricity	266	4.15%	11
Water	3	4.15%	0
Rent	83	4.15%	3
Rates	66	4.15%	3
	450		**19**
Security	47	4.15%	2
	47		**2**

The apportionment for each magnetic ink, including a price per kilo for manufacturing each formulation is held within the accounts department at BBP. Table 6.6 gives a summary cost, accounting for the apportionment of each product, and giving a generic price per kilogram for slurry manufacture in HMI based on projected annual forecast and current supplier raw material prices. Please note that due to recent qualification of HL0501 and HH0307, they have not been included in the financial calculations as the predicted forecast for these products is to be confirmed, however combined it is not likely to exceed 10 tonnes and so the overall picture is unlikely to be hugely different.

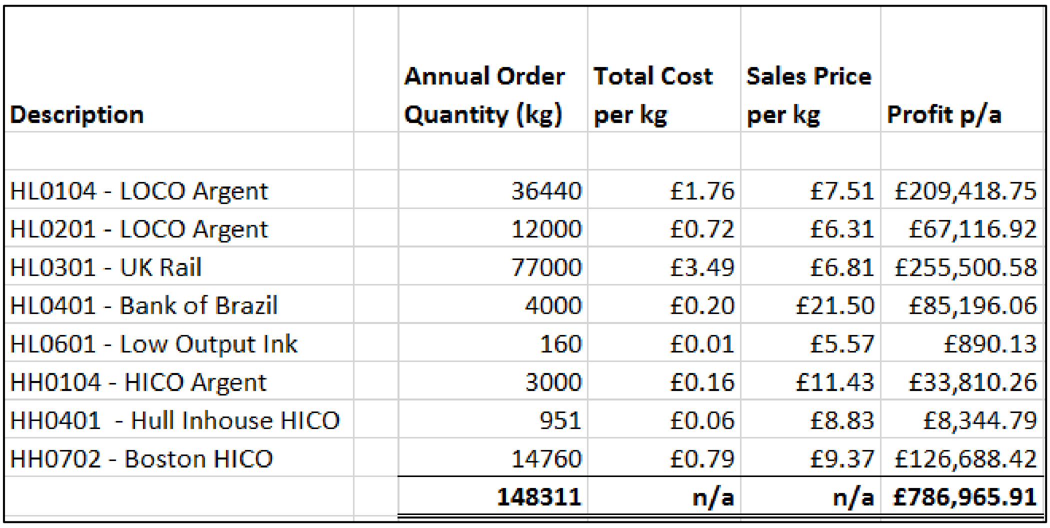
Table 6.6: Summary of total ink manufacturing cost.



Summary					
Approx 148311		Exchange rate	1.17	**GBP'000 / year**	**EUR'000 / year**
Depreciation					
Machines	*2 * 100S £250k / 1 * 60S £250k / 2 *30S £120k / 2 * Resin Mixes £20k Over 5 Year*			206	241
Others	*All other HMI Costs 3 years*			22	26
Subtotal Depreciation				**228**	**267**
Direct Labour					
Machine Conductors	*100 % 2 operators = 2 FTE*			29	34
Subtotal Direct Labour				**29**	**34**
Other Remuneration costs					
R&D	*100 % Haydn Ward = 1 FTE*		Formulas pulling from salary tab	33	39
Production Mgr	*5 % Graham Winship = 0,05 FTE*		Formulas pulling from salary tab	3	3
Quality	*100% Tracy Harrison = 1 FTE*		Formulas pulling from salary tab	19	22
Planning Manager	*15 % Martin Waudby = 0,15 FTE*		Formulas pulling from salary tab	6	7
Planning Assistant	*20% Robert Bassett = 0,20 FTE*		Formulas pulling from salary tab	4	5
Supervisor	*5% Steve Marritt = 0,05 FTE*		Formulas pulling from salary tab	1	2
Technical Manager	*5% Jamie Parker = 0,05 FTE*		Formulas pulling from salary tab	2	2
Subtotal ORC				**68**	**77**
Other Manufacturing Expenses (OME)					
Freight	Freight			12	14
Repairs & Maintenance	*Direct cost*			16	19
Welfare	*Health & Safety / Clothing - Direct HMI Code*			12	14
Professional Fees	*Direct Overhead - Consultants/Other Professional Fees - Other Professional Fees*			45	52
Other	*Training, Cleaning, Equipment Rentals*			24	28
Allocation / Floor space - 4.15% (270/6503 s	*Security*			2	2
Allocation / Floor space - 4.15% (270/6503 s	*Rent / Rates / Utility*			19	22
Subtotal OME				**129**	**151**
Total Manufacturing costs Exc Materials				**454**	**530**
Cost Per Kilo				**3.06**	**3.58**
Material Costs per kilo					
Total Material Cost				302	353
				302	**353**
Total Manufacturing costs inc Material Costs				**756**	**882**
Cost Per Kilo				**5.10**	**5.96**

The sales price of each ink is detailed in Table 6.7 below. The margins are variable in some cases due to intercompany sales vs export to an external customer for example. The figure is relative to site floor space of HMI, including capital depreciation at full replacement cost.

Table 6.7: Annual Magnetic Ink profitability based on Full Capital replacement.



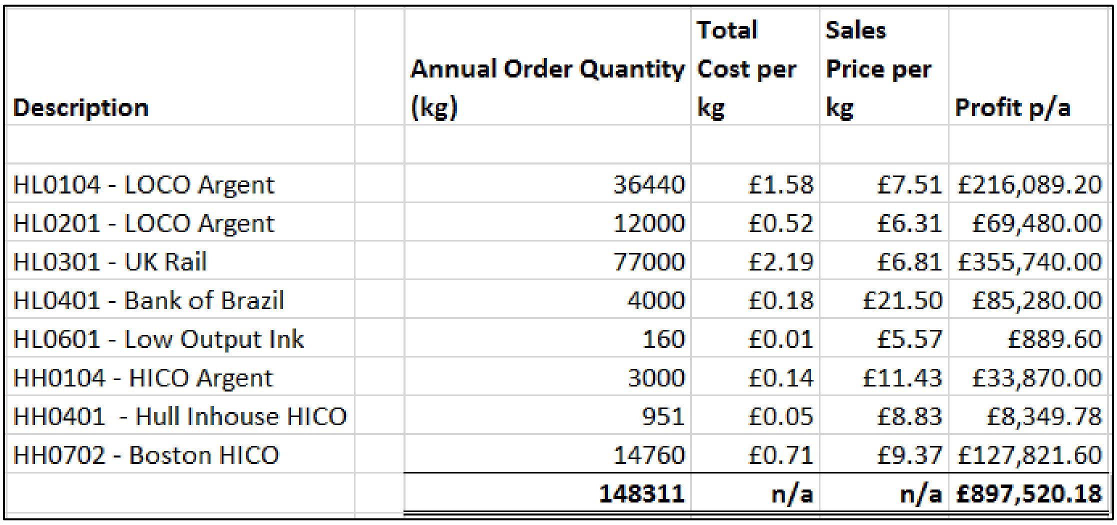
Description		**Annual Order Quantity (kg)**	**Total Cost per kg**	**Sales Price per kg**	**Profit p/a**
HL0104 - LOCO Argent		36440	£1.76	£7.51	£209,418.75
HL0201 - LOCO Argent		12000	£0.72	£6.31	£67,116.92
HL0301 - UK Rail		77000	£3.49	£6.81	£255,500.58
HL0401 - Bank of Brazil		4000	£0.20	£21.50	£85,196.06
HL0601 - Low Output Ink		160	£0.01	£5.57	£890.13
HH0104 - HICO Argent		3000	£0.16	£11.43	£33,810.26
HH0401 - Hull Inhouse HICO		951	£0.06	£8.83	£8,344.79
HH0702 - Boston HICO		14760	£0.79	£9.37	£126,688.42
		148311	**n/a**	**n/a**	**£786,965.91**

As the machines were bought second hand, the above table is not representative of the actual costs paid, and so the figures containing actual depreciation values have also been produced in Tables 6.8 and 6.9.

Table 6.8: Summary of ink manufacturing cost including actual depreciation values.

Summary					
Approx 148311		Exchange rate	1.17	**GBP'000 / year**	**EUR'000 / year**
Depreciation					
Machines	*See Asset Register (£103k)*			25	29
Others	*All other HMI Costs - See Asset Register (£30k)*			13	15
Subtotal Depreciation				**38**	**44**
Direct Labour					
Machine Conductors	*100 % 2 operators = 2 FTE*			29	34
Subtotal Direct Labour				**29**	**34**
Other Remuneration costs					
R&D	*100 % Haydn Ward = 1 FTE*		Formulas pulling from salary tab	33	39
Production Mgr	*5 % Graham Winship = 0,05 FTE*		Formulas pulling from salary tab	3	3
Quality	*100% Tracy Harrison = 1 FTE*		Formulas pulling from salary tab	19	22
Planning Manager	*15 % Martin Waudby = 0,15 FTE*		Formulas pulling from salary tab	6	7
Planning Assistant	*20% Robert Bassett = 0,20 FTE*		Formulas pulling from salary tab	4	5
Supervisor	*5% Steve Marritt = 0,05 FTE*		Formulas pulling from salary tab	1	2
Technical Manager	*5% Jamie Parker = 0,05 FTE*		Formulas pulling from salary tab	2	2
Subtotal ORC				**68**	**77**
Other Manufacturing Expenses (OME)					
Freight	Freight			23	27
Repairs & Maintenance	*Direct cost*			9	11
Welfare	*Health & Safety / Clothing - Direct HMI Code*			16	18
Professional Fees	*Direct Overhead - Consultants/Other Professional Fees - Other Professional Fees*			24	28
Other	*Training, Cleaning, Equipment Rentals*			14	16
Allocation / Floor space - 4.15% (270/65	*Security*			2	2
Allocation / Floor space - 4.15% (270/65	*Rent / Rates / Utility*			10	11
Subtotal OME				**97**	**113**
Total Manufacturing costs Exc Materials				**232**	**269**
Cost Per Kilo				**1.56**	**1.83**
Material Costs per kilo					
Total Material Cost				302	353
				302	**353**
Total Manufacturing costs inc Material Costs				**533**	**622**
Cost Per Kilo				**3.59**	**4.21**

Table 6.9: Profit calculation using actual depreciation values.



Description		**Annual Order Quantity (kg)**	**Total Cost per kg**	**Sales Price per kg**	**Profit p/a**
HL0104 - LOCO Argent		36440	£1.58	£7.51	£216,089.20
HL0201 - LOCO Argent		12000	£0.52	£6.31	£69,480.00
HL0301 - UK Rail		77000	£2.19	£6.81	£355,740.00
HL0401 - Bank of Brazil		4000	£0.18	£21.50	£85,280.00
HL0601 - Low Output Ink		160	£0.01	£5.57	£889.60
HH0104 - HICO Argent		3000	£0.14	£11.43	£33,870.00
HH0401 - Hull Inhouse HICO		951	£0.05	£8.83	£8,349.78
HH0702 - Boston HICO		14760	£0.71	£9.37	£127,821.60
		148311	**n/a**	**n/a**	**£897,520.18**

It is evident that from both profit calculations HMI is very much a profitable area of the site, and has indeed been a successful start-up business within BBP. The associated risks were also identified and logged for this area of the project and can be found in Appendix 8.

Having developed (1) the ink formulations (Chapter 4), (2) the ink manufacturing process plant (Chapter 5) and identified the favourable economics for the manufacturing process (this chapter), the next chapter examines several types of magnetic ink developments. Specifically (1) development of a correlation between the VSM and BH Looper measurements which were instrumental in qualifying FHL0201 for the RATP (Paris Metro); (2) the blending of inks and pigments to qualify HL0104 for the French motorways and overcome issues with HL0103; (3) the use of strontium ferrite to develop a suitable Pyral H400 slurry replacement as HH0307; (4) the development of environmentally friendly “mAquetic” ink and (5) solvent evaporation rate measurements as a QA/QC tool for traceability post-manufacture and.

Chapter 7 – Magnetic Ink Developments

Several formulation development programmes were undertaken to drive the success of this project. They were.

- FHL0201 development – correlation between systems
- HL0104 development – blending of pigments
- HH0307 development – Identifying SrFe as the correct HiCo pigment
- Water Based ‘mAquetic’ ink development
- QA/QC of inks through solvent evaporation kinetics.

7.1 Development of FHL0201 and HL0104

The main criterion for successful qualification of magnetic ink is that, when the ink is coated, oriented and dried to form a thin film on a substrate, it exhibits correct magnetic characteristics in terms of the coercivity, squareness and switching field distribution. These have to match up with those required by the ink specification.

In starting-up production runs, it was essential to ensure that the magnetic properties (specifically coercivity) tested through un-oriented manual draw-downs onto a polyethylene terephthalate (PET) substrate on a vibrating sample magnetometer (VSM) would match-up with the oriented thin films of the produced coated board tested on a BH looper.

Table 7.1: Magnetic characteristics of coated reference samples using a BH looper.

	BH Looper Data		
Sample	**Hc/Oe**	**Sq**	**SfD**
H400 Pyral Paper Oriented	3339	0.8582	0.761
HH0301 PET Unoriented	3511	0.743	0.5506
H270 Pyral Paper Oriented	2676.5	0.7348	0.41675
HH0104 PET Unoriented	2664	0.73795	0.48645
H270 Pyral PET Oriented	2586	0.785	0.39815
HH0401 Paper Oriented	2614	0.71995	0.564
HL0301 Paper Oriented	362.2	0.72935	0.579
HL0104 Paper Oriented	352.55	0.76895	0.51575
FHL0201 Paper Oriented	350.3	0.76605	0.59165
HL0301 PET Unoriented	334	0.76415	0.6509

Accordingly, in order to develop a pragmatic working correlation between these two different testing processes and protocols, a series of measurements on the VSM were compared with data obtained on similar cuts from the samples on the BH looper. A key part of this correlation required a set of standard, quality assured, production samples to be tested between the two systems. However, since the nature of the coated board (substrate) may affect

These data are indicated in Table 7.1, where it is clear that there is a substrate effect of a maximum of 6% in coercivity change between the coated and drawn-down samples.

Having identified a substrate effect, attention was next focused on the change in reported coercivity between the VSM and BH looper on un-oriented, manual drawn-down samples on PET. This is illustrated in figure 7.1 for the first three production batches that were manufactured during the KTP, corresponding to magnetic ink HL0103.

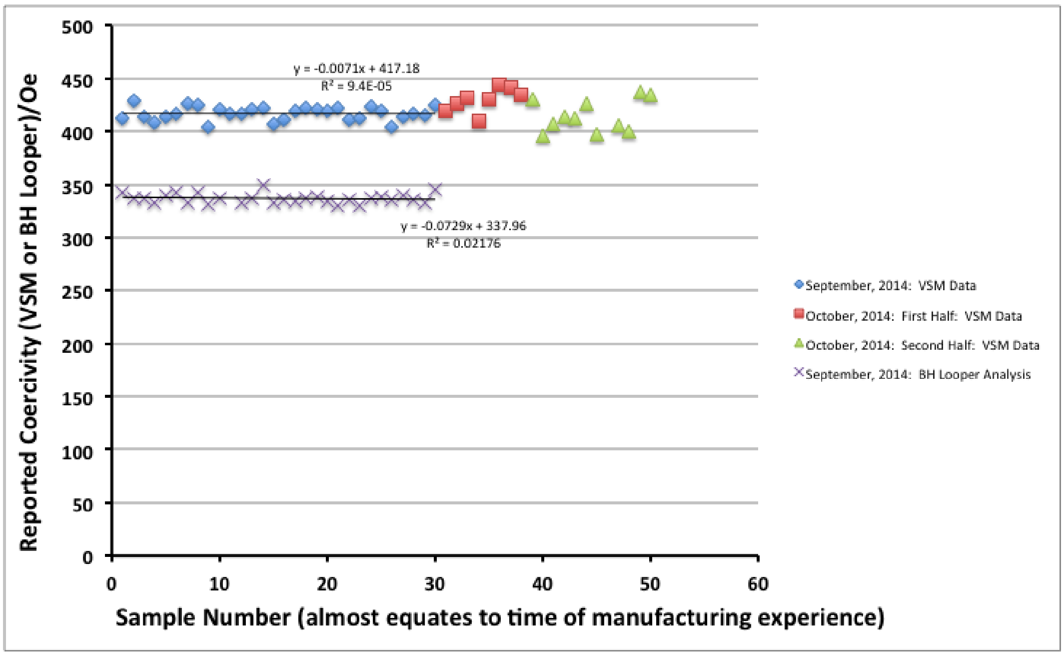


Figure 7.1: Shewhart chart of coercivity for HL0103 as a function of manufacturing experience.

It is evident from these data that there are substantial differences between the reported BH looper analyses and those extracted from VSM measurements. In order to identify whether this had resulted from poor data handling protocols of the VSM data in Microsoft Excel, the latter were reanalyzed using Mathematica and Matlab (see Appendix 9 for a copy of the Matlab Script File employed). These confirmed the trends in coercivity depicted in figure 7.1, from where it is seen that VSM measurements are typically *ca.* 80 Oe larger in coercivity than those measured by the BH looper. Note that the data on squareness and switching field distribution could not be found to correlate, as these are a function of the sampling process.

In considering BH looper data on un-oriented, manual draw-down on PET to oriented, coated board, there is a 6% maximum increase in coercivity, thereby enabling the following phenomenological correlation to be suggested.

$$\left(Hc/Oe\right)^{oriented\ coated\ board}_{BL\ looper} = 1.06\left\{\left(Hc/Oe\right)^{unoriented\ draw\text{-}down}_{VSM} - 80.3\right\} \qquad \text{Eq. 7.1}$$

The verification of this working correlation is illustrated in Table 7.2.

Table 7.2: Correlated prediction of the manufactured slurries.

Sample	Hc VSM DD/Oe	Hc PID DD/Oe	VSM corrected/Oe	Hc Prediction/Oe	Hc coated board/Oe	Comments
September FHL0103	417.1	336.8	336.8	357.0	354-356	Prediction matches
October FHL0103	414.9		334.6	354.7	354-355	Prediction matches
December HL0201		326.1		345.7	339	Prediction approximately matches

This correlation was used for the qualification of FHL0201 (magnetic ink for RATP): a measured coercivity of un-oriented ink drawn-down onto PET of 326.1 Oe was predicted to be 345.7 Oe (maximum) for coated, oriented samples. Production runs identified Hc = 341 Oe, which is well within the specification of 335 ± 12 Oe.

The development of fully qualified HL0104 ink relied on the correct coercivity of the pigment, as well the correct reconditioning of otherwise waste product (HL0103). Both aspects are next considered in turn.

First, the specification for the ink required the coercivity to be 315 ± 25 Oe. However, manufactured HL0103 appeared to yield coercivities of 337 ± 4 Oe (see figure 7.1), which was too high. Moreover, in using this ink, holes started to appear in the magnetic stripe due to slurry being deposited on the calendar roller and on the smoothers (figure 7.2). Furthermore, the slurry was found to be inhomogeneous, periodically gelling inside the left-hand driven rotogravure printer (figure 7.3).

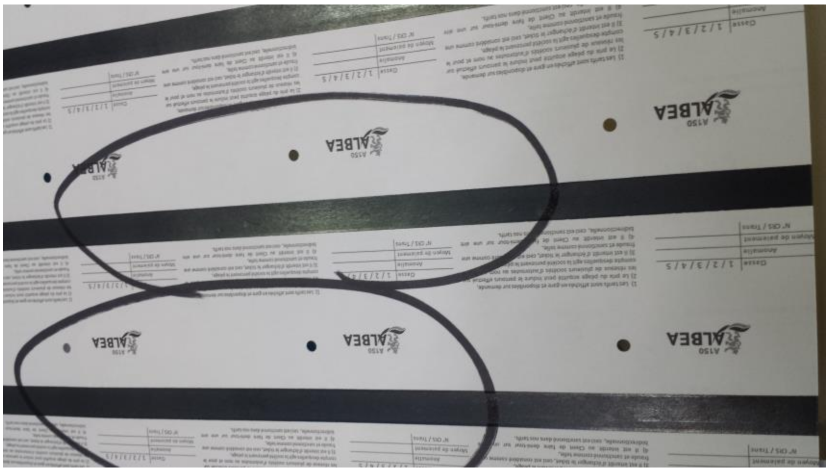


Figure 7.2: Holes in the magnetic stripe due to deposits on the calendar roller.

Figure 7.3: Gelling of HL0103 inside the printing machine

To overcome the issues associated with HL0103, a new slurry formulation was conceived to replace HL0103, involving the removal of carbon black (which, with high oil absorption and high surface area) was considered to encourage gelling, and replacing 25% of the ferrimagnetic pigment (of coercivity 320 Oe) with a similar-sized and shaped pigment, albeit of lower coercivity (310 Oe). Pleasingly, production trials of the resulting printed slurry, HL0104, which was observed to print at normal running speeds (60 m/min) identified a coercivity of 328 Oe, squareness of 0.75 or higher, and SF_D of 0.54 or lower. This slurry was commissioned for French motorway tolls, initially trialed live by Sanef in the North-East region of France. Typical manufacturing runs afford the data depicted in figure 7.4.

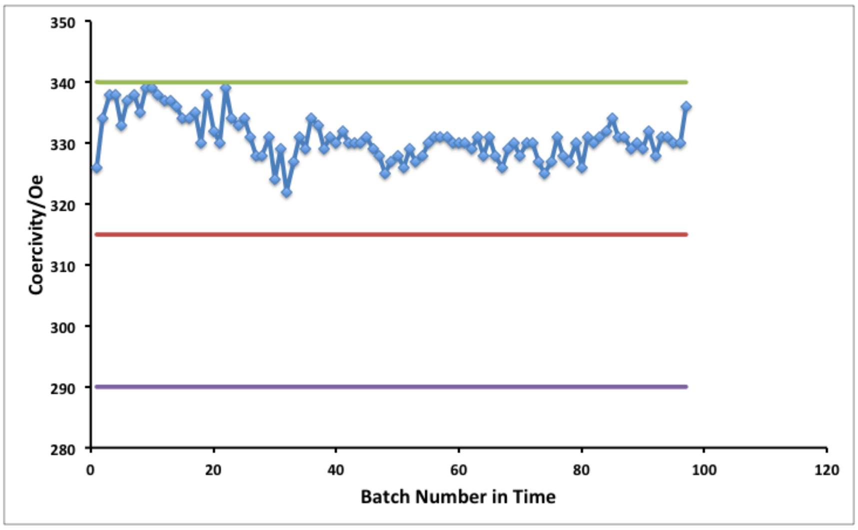


Figure 7.4: Shewhart chart for HL0104 manufacturing between April-July, 2015. The lines represent mean ± limit of the specification.

Notwithstanding the fact that successful slurry development had taken place, in order to ensure cost-effective recycling of 9.2 tonnes of wasted, non-qualified HL0103 ink, small scale experiments were undertaken to blend HL0103 with the successfully qualified HL0104, using the mini-mixer mill. The results of the proofed and oriented inks on PET are shown in figure 7.5, where it is seen that below a 50:50 blend, the ink falls into the upper limits of the specification.

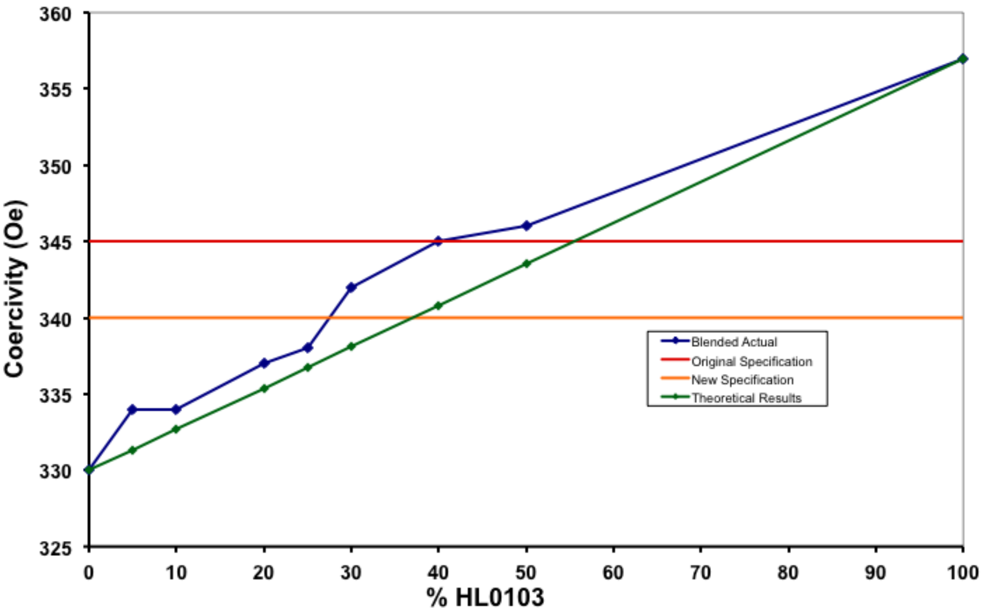


Figure 7.5: Effect of blending HL0103 with HL0104 on the coercivity of the resulting ink.

For manufacture scale, in order to ensure the efficient and rapid reuse of the slurry, HL0105 was manufactured using 25% of the pigment with coercivity 310 Oe, and 75% of a pigment with coercivity of 300 Oe, with the remainder of the ink being the same as HL0104. This new slurry was bended with the non-conforming HL0103 slurry, to afford one, which held good flow and vast improvement, in specification magnetic characteristics.

Having developed a route to modulate and fine-tune the properties of low coercivity magnetic ink, attention is next focused on developing high coercivity ink to an extremely tight specification.

7.2 Development of HH0307

Strontium, barium and cobalt ferrites are known as ‘hard’ ferrites as they possess a much higher coercivity and are therefore much harder to demagnetize. These ferrites have a hexagonal crystal structure in comparison to the acicular ‘needle’ type particles observed in softer ferrites such as maghemite/magnetite. Strontium ferrite is mainly used in the manufacture of magnets, however is also of vital use in the magnetic recording industry for ‘HiCo’ products. The importance of using the compound to achieve a final product with a high squareness and low switching field distribution (SF_D), whilst retaining a high coercivity have become prevalent in recent attempts to manufacture such a formulation in magnetic ink slurry format. Unfortunately, global supplies of strontium ferrite – without the additives required for magnet production included during large scale chemical manufacturing – seem to be extremely limited. The search for a consistent supply of the compound in its pure form with the correct magnetic characteristics is ongoing.

A competitor’s product (Pyral, H400) had previously been in line with the required specification ($Hc = 3500 \pm 270$; squareness ≥ 0.8; $SF_D \leq 0.7$), in accordance with ISO 15457-2:2007(E). However, as indicated herein, the product has drifted out of specification in recent times. It was believed that this is due to a change in the strontium ratio within the formulation, likely to be due to an exhausting supply. The strontium ferrite pigment has been replaced with the more readily available barium ferrite. However, if this is not undertaken in the correct stoichiometric ratio, it elicits a detrimental effect on the characteristics of the final product, specifically squareness and SF_D.

The scientific reasoning behind this is based on the ionic radius of strontium being smaller than that of barium. If the platelets coexist more closely together due to the smaller strontium cation, this may account for an increase in the squareness, and a decrease in the SF_D. The SF_D is a distribution of the intrinsic coercivities of the particles in the slurry. The squareness is the ratio between the remenant magnetization and the saturation magnetization, this in itself is dependent on the maximum field applied and is reduced when the SF_D increases. Higher squareness ratios are achievable with particles being evenly distributed in a small solid angle around the orientation direction, so that it becomes important to have within any slurry system as much of one type of pigment particle present.

The key features outlined herein have identified that the current Pyral H400 product (which utilizes a mixture of barium and strontium pigments) is out of specification for squareness and SF_D, whilst the BBP product is only out of specification on squareness (barium pigment only). As the strontium to barium ratio decreases, SF_D and squareness move out of specification. The results of a BBP product (HH0307) manufactured using strontium ferrite are subsequently presented.

The raw pigments express their magnetic behaviour due to the structure and interactions of the chemical compound. Ferrites are magnetic materials which exhibit ferrimagnetic properties. A ferrimagnetic material contains populations of atoms with unequal and opposing magnetic moments, thus creating a lasting spontaneous magnetization (*i.e.* Fe^{2+} and Fe^{3+} ions within the same environment).

Barium and strontium ferrites also hold ferrimagnetic properties however the particle shapes are of a hexagonal crystal structure, resulting in strong uniaxial magnetocrystallin anisotropy. All of the iron in this system is of the Fe^{3+} form. The structure (P63 space group) consists of FeO_6 octahedra and FeO_4 tetrahedra with the barium ions in 12-coordinate sites between. The unit cell contains four FeO_4 tetrahedra to 32 FeO_6 octahedra – therefore for every tetrahedron there are eight octahedra. This structure can be observed in figure 7.6. Ferrimagnetism occurs through the pairwise combinations of the octahedra and tetrahedral magnetic domains. Pure barium ferrite has coercivities in the range 2-3 kOe and a coercivity which unusually tends to decrease with increasing temperature (by 4.8 Oe K^{-1}. The platelet aspect of the barium ferrite crystals empower their suitability as media for perpendicular readings.

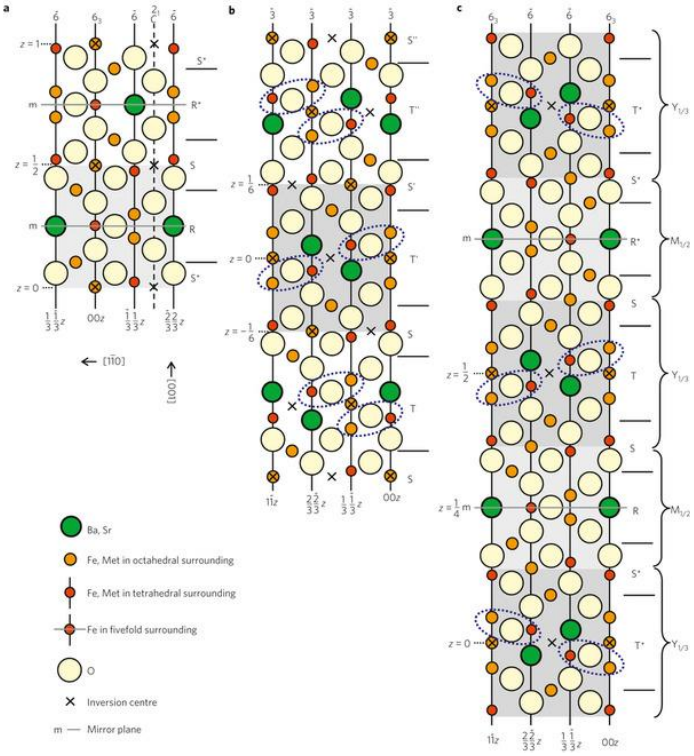


Figure 7.6: Structure of barium/strontium ferrite [1].

An initial SEM experiment on the barium ferrite pigments was carried out to obtain the shape and condition/consistency of the pigment particles and to determine purity. High resolution images from the experiment can be seen below in figures 7.7 and 7.8; they show a maghemite pigment and a pure barium ferrite pigment respectively.

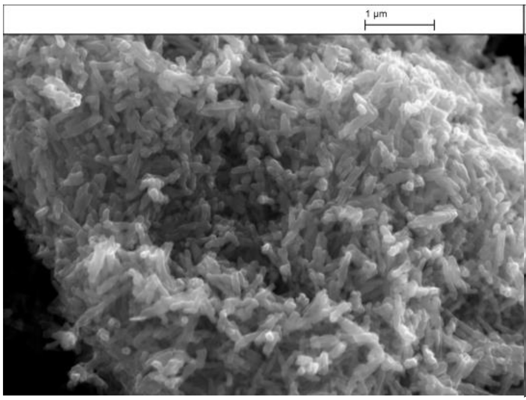


Figure 7.7: 'Needle' type maghemite (Coercivity 305-330 Oe)

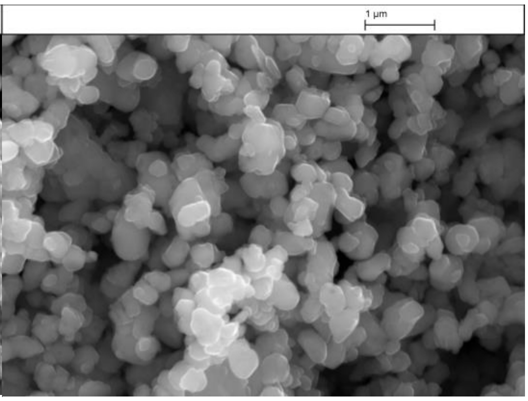


Figure 7.8: 'Hexagonal' type barium ferrite (Coercivity 3500 Oe)

Although the structure remains the same, the contribution of barium ferrite and strontium ferrite towards the final magnetic properties must be determined accordingly, to verify this hypothesis an investigation into the correlation of strontium/barium content within Pyral formulations and the magnetic characteristics *via* SEM and BH Looper analyses was undertaken.

Attempts to produce a formulation with the same characteristic as the Pyral H400 were originally made using 100% of the more readily available barium ferrite. The results were positive in specification for all characteristics apart from magnetic squareness. The results of the first two trials using this pigment are shown in Tables 7.3 and 7.4 below.

Table 7.3: Results of first H400 Ferron trial – FHH0201.

Sample	1	2	3	4	5	Average
Applied Field Hm: (15000 ± 200 Oe)	14884	14841	14766	14771	14718	14796
Coercivity, Hc: (3500 ± 270 Oe)	3422	3455	3389	3476	3482	3445
Saturation:	16396	15431	17595	16317	16623	16472
Remanence:	11337	10443	11170	11537	11755	11248
Squareness: (≥ 0.8)	0.6914	0.6768	0.6349	0.707	0.7072	**0.6835**
Sf_D: (≤ 0.7)	0.5383	0.5294	0.5489	0.551	0.5343	0.5404

Table 7.4: Results of second H400 Ferron trial – FHH0202.

Sample	**1**	**2**	**3**	**4**	**Average**
Applied Field Hm: (15000 ± 200 Oe)	14930	14979	15032	14868	14952
Coercivity, Hc: (3500 ± 270 Oe)	3357	3354	3385	3356	3363
Saturation:	17891	18568	18619	17929	18252
Remanence:	12470	13244	13059	13090	12966
Squareness: (≥ 0.8)	0.6970	0.7133	0.7014	0.7301	**0.7105**
Sf$_D$: (≤ 0.7)	0.6640	0.6884	0.6591	0.6632	0.6687

It is clear from tables 7.3 and 7.4 that the squareness is inadequate. Trial 2 (FHH0202) was tested and a direct comparison was made with a Pyral H400 production sample (date of this production is unknown). Trial 2 involved alterations in the manufacturing process parameters in order to attempt to improve final product squareness. The results of the Pyral production sample are excellent in comparison with the specification as shown in table 7.5.

Table 7.5: Pyral in specification production results.

Sample	**1**	**2**	**3**	**Average**
Applied Field Hm: (15000 ± 200 Oe)	15077	15046	15059	15061
Coercivity, Hc: (3500 ± 270 Oe)	3319	3321	3322	3321
Saturation:	13969	14492	13577	14013
Remanence:	12312	12043	12001	12119
Squareness: (≥ 0.8)	0.8814	0.831	0.8839	0.8654
Sf$_D$: (≤ 0.7)	0.6863	0.6445	0.6914	0.6741

The alteration of manufacturing parameters achieved a small improvement in the squareness and there is further scope for improvement. However, it is expected that the tolerance levels required are unachievable, even by exploring the maximum limits, using barium ferrite only. Based on this outcome it was suspected that the difference in the formulations causing a large deviation in the Ferron trial is most likely to be the raw pigment and its properties. In order to determine this for certain, SEM was carried out on various samples to observe any elemental formulation difference and trend in data. SEM data are subsequently compared with magnetic data to determine if there are any effects from the observed alterations. Table 7.6 identifies the samples analyzed during this process.

Table 7.6: Samples analyzed, by method, and the date of slurry manufacture.

Sample	**Description**	**Analysis**	**Slurry Manufacturing Date**
A	H400 latest coated sample.	BH Looper	December 2014
B	H400 coated sample (obtained July 2014).	SEM BH Looper	Unknown
C	H400 coated sample 2 (obtained December 2014)	SEM BH Looper	Unknown
D	FHH0202 coated Ferron trial	SEM BH Looper	November 2014
E	H400 sample poor viscosity	SEM	Unknown
F	H400 sample good viscosity (latest obtained)	SEM	Unknown
G	H400 draw-down of same batch as sample 0.	SEM	December 2014

BH Looper results for sample A were obtained on January 29, 2015 and are poor in relation to the specification. The results (table 7.7 below) show that the production sample is below the allowable squareness tolerance (≥ 0.8) at 0.7662, and above the allowable tolerance for SF_D (≤ 0.7) at 0.7706. Sample B obtained in July (manufacture date unknown) showed a sample with an improved result compared with the specification however SF_D was not within the allowable tolerance, at 0.7610 (see table 7.7). Sample C obtained in December (manufacture date unknown) was perfectly within specification (table 7.5). In order to justify these results SEM was undertaken on the relevant samples to determine the reason for this shift in magnetic data.

Table 7.7: BH Looper data for sample A.

Sample Reference	Description	Temperature (C)	Coercivity Hc (Oe)	Squareness	SFD
Tolerance	Allowable parameters	n/a	3500+/-270	>0.8	<0.7
A(1)	H400 Pyral Coated (B14043022/7074)	n/a	3264	0.7831	0.7715
A(2)	H400 Pyral Coated (B14043022/7074)	n/a	3242	0.7493	0.7697
B	H400 Pyral Coated (Obtained July 2014)	n/a	3339	0.8582	0.7610

SEM-EDX data for sample G (draw-down of same slurry batch as sample A) identify that both strontium and barium ferrites are present within the formulation. This was deduced through examining the compositional ratios of iron to strontium and barium present within the dried slurry. In considering the chemical formulae for barium ferrite ($BaFe_{12}O_{19}$) and strontium ferrite ($SrFe_{12}O_{19}$) empirical stoichiometric equivalence of Ba to Fe and Sr to Fe were calculated. The stoichiometric ratio shows that strontium is present as 3:1 with barium (75% strontium, 25% barium), yielding an out of specification product.

In order to determine whether this ratio had changed through the H400 production history, SEM-EDX was subsequently carried out on the previously obtained samples of H400 to correlate specification with pigment.

Sample B was found to contain a stoichiometric ratio of strontium to barium of 3.5:1 (77.5% strontium and 22.5% barium), and this product, as above, was out of specification for SF_D. Sample C was tested on the SEM, producing a stoichiometric ratio of strontium to barium of 4:1 (80% strontium, 20% barium); this is out of specification for squareness as documented in table 3. As expected the results of FHH0202 (barium content known) gave a value of 100% barium (sample D). Samples E and F confirmed the ratio of strontium to barium alters but these are samples that have not had their magnetic characteristics examined.

It is clear from the results observed from the SEM-EDX investigation with magnetic characterization that Pyral's samples range from first performing within specification and move out of the specification. The argument made herein that this relates to the strontium ferrite content appears to be substantiated; to illustrate this, figures 7.9 and 7.10 display how squareness and SF_D alter respectively on a sample basis. Unfortunately the manufacture date is not traceable through PID, only a BBP received date which is not likely to be relevant.

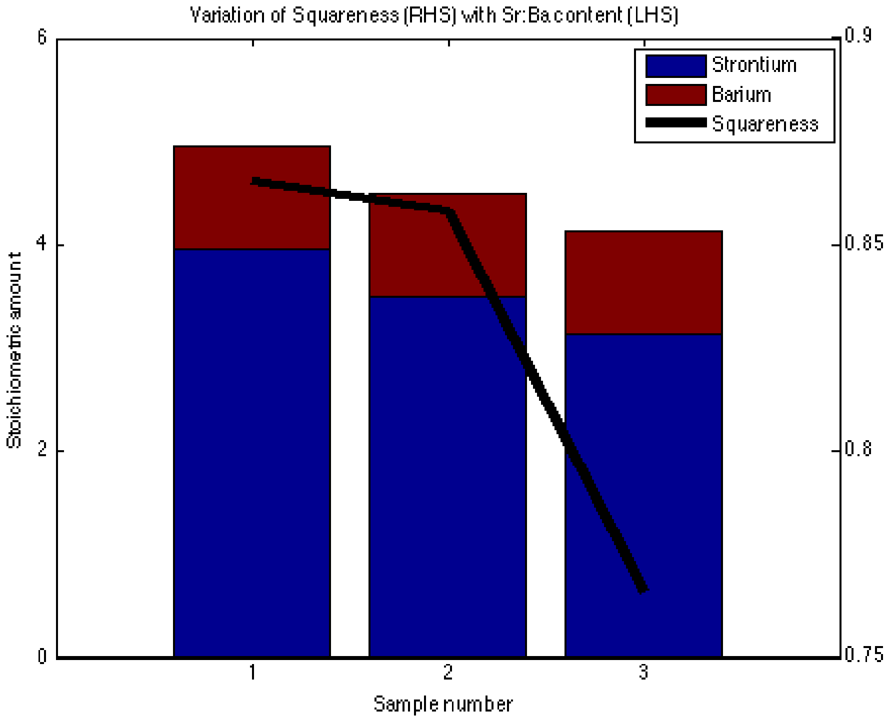


Figure 7.9: Effect of stoichiometric strontium reduction on sample squareness. KEY; sample 1 = C, 2 = B and 3 = A

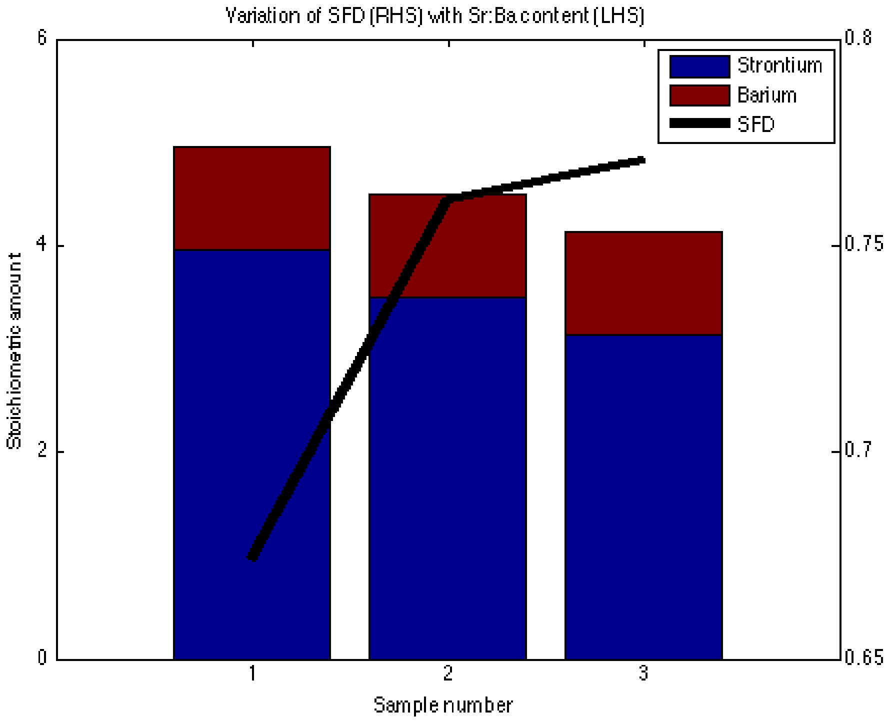


Figure 7.10: Effect of stoichiometric strontium reduction on sample SF$_D$. KEY; as for figure 6.

The above results show a definitive trend and strongly appear to be related to the strontium content. In figures 7.9 and 7.10 the stoichiometric equivalent of barium is constant whilst the strontium content increases moving from samples '1 to 3'. The decrease in the strontium content is manifested through the increase in the SF$_D$, and as expected a reduction in the squareness: as the amount of strontium content (compared with barium) in the formulation decreases, the product drops further out of the specification for squareness and SF$_D$.

The change in SF$_D$ can be accounted for due to the mixture in pigments in the H400 formula. It appears that at a lower level of mixing (20% barium) the effect is not observed however becomes magnified as the mixture ratio is progressed more closely to 1:1. Inasmuch as strontium ferrite and barium ferrite hold similar crystal structures, the smaller ionic radius of strontium compared with barium identifies a greater pull on the iron oxide octahedra and tetrahedra within the P63 space group. This in itself is likely to result in a more uniform alignment of the pigment upon orientation in the final slurry product.

There is a relationship between the strontium content of the H400 formulation and the specification tolerance of the magnetic characteristics of the formulated slurry. It is evident that as the strontium to barium stoichiometric ratio is decreased, the squareness and SF_D drift out of the allowable tolerances. This decrease in the ideal ratio due to a drop-in strontium is highly likely to be related to the currently limited global supply of strontium ferrite (attempts to source this compound with the correct characteristics are ongoing): Pyral appear to be attempting to extend the life of an exhausting supply by reducing the relative amount within their formulation. 17, 5, 23

Currently the BBP FHH0202 product (H400 equivalent) performs to specification on a level higher than that of Pyral's H400: FHH0202 is within specification on coercivity and SF_D but out of specification on squareness; H400 however is in specification on coercivity, but out of specification on both squareness and SF_D.

The attempts to secure a reliable supply of strontium ferrite of a suitable grade have hitherto proved futile. There are several routes forward in the case that no suitable strontium ferrite is able to be sourced. One of these routes includes the adjustment of the specification for the customer and the forward supply chain. Alternatives do exist. These will all be detailed within a report following further investigations.

The results of the latest trial of H400 equivalent product (HH0307) using a strontium ferrite pigment sourced on the market have given the best possible results, hitting the ISO standard requirements for every parameter and, specifically, $Hc = 3581$ Oe, $Sq = 0.8517$ and $SF_D = 0.4784$.

7.3 "mAquetic" Inks: Water Based Magnetic Ink

Magnetic ink currently produced in HMI at BBP is dependent on the use of volatile organic compounds for the formulation vehicle. In recent times, due to both business acquisitions and success in tender bids, the manufacturing and coating volumes within BBP have risen by a huge proportion. This does not only strain the current environmental permit due to VOC emission limits, but also increases risk and hazard in terms of process safety due to the increased volume of flammable product being handled. There are also further implications in terms of potential eligibility for COMAH regulations if the volume of solvent stored on site reaches a level that surpasses the minimum.

An ideal solution to this would be to remove VOC compounds from all manufacturing and produce magnetic inks in a water-based medium. There are several advantages to this aside from the obvious reduction in VOC emissions, particularly the reduction in the level of PPE required for manufacturing and also the removal of an expensive to maintain ATEX rated process room. Unique marketing opportunities would surface from the successful production of a water-based magnetic ink, named by BBP as ‘mAquetic’ ink.

There are many challenges associated with the development of a fully functional production scale water based magnetic ink, especially when formulating from the ground-up. The process must be planned in stages, achieving various milestones during the progression of the project.

Challenges in ‘mAquetic’ ink manufacture initially include the production of an ink with the correct magnetic properties. Once the correct magnetic properties have been achieved, a stable and consistent dispersion must be obtained. The chemistry of the formulation must then be considered in terms of coating and drying properties. Substrate ingress will be an issue along with drying time of the water-containing ink. Water also has a higher surface tension, meaning a magnified tendency to foam on the addition of surfactant components; this must be addressed as a processing issue.

Water-containing magnetic inks have been produced previously by other global ink manufacturing competitors. One benchmarking sample obtained by BBP was a tin of Pyral's WL330 magnetic ink. This was characterized, obtaining results for solid content, viscosity, dispersion and magnetic/electrical levels.

The results of this ink characterization drawn down on both paper and polyester are in Table 7.8 below.

Table 7.8: Pyral water-based slurry results.

Pyral Water Based LoCo Slurry					
Sample on Paper	**% Torque**	**Viscosity (cP)**	**SQ**	**SFD**	**Hc (Oe)**
1	67.5	2700	0.751	0.504	335
2	67.5	2700	0.738	0.510	334
3	67.5	2700	0.753	0.498	337
Sample on Perspex	**% Torque**	**Viscosity (cP)**	**SQ**	**SFD**	**Hc (Oe)**
1	67.5	2700	0.755	0.478	333
2	67.5	2700	0.745	0.504	336
3	67.5	2700	0.758	0.495	337
4	67.5	2700	0.770	0.498	337

Figure 7.11 shows the consistency of the ink formulation.

Figure 7.11: Pyral WL330 water based magnetic ink.

A Mag3 electromagnetic trace was completed on the sample, and in addition to formulation stability, the WL330 represented positive readings in relation to ISO 7811-2. Figures 7.12 and 7.13 show the manual draw down and corresponding trace.

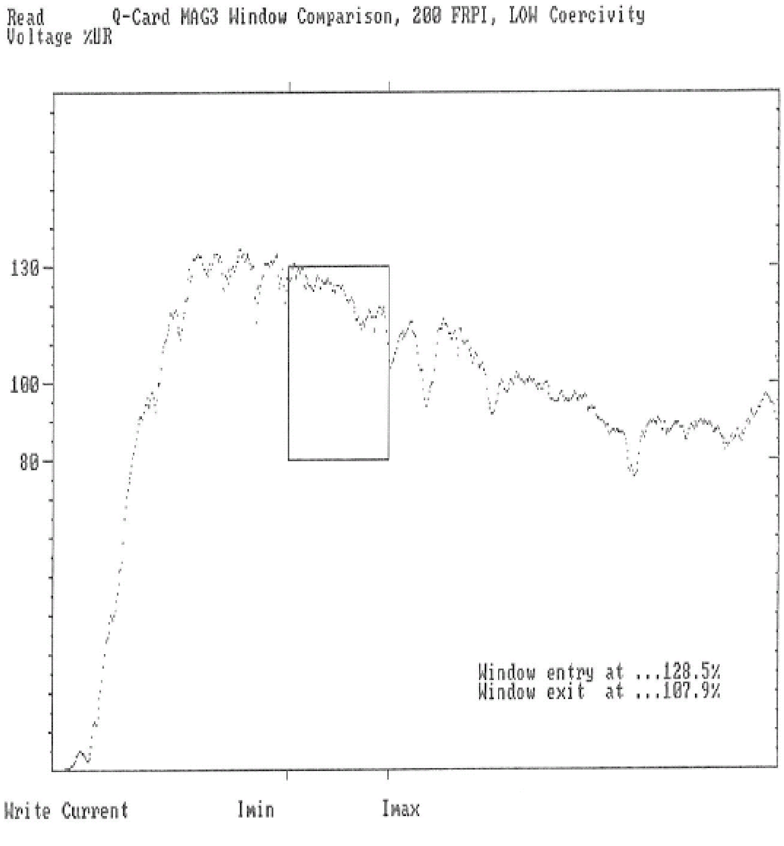


Figure 7.12: WL330 Mag3 trace on manual draw-down.

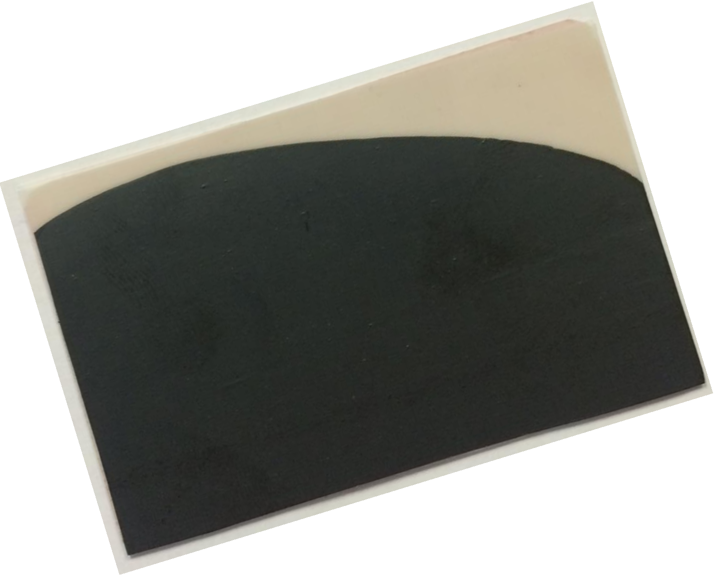


Figure 7.13: WL330 draw down.

The positive results obtained by this product encouraged the production of a water based magnetic ink at HMI that is capable of passing all required quality assurance tests.

In order to innovate on this competitor product, first, a formulation with functional magnetic properties must be obtained, ignoring any stability or dispersion issues. To achieve this, two major formulation routes were devised. One from an 'emulsion' based chemical system involving self-cross-linking polymers, and another through an aldol based chemical condensation reaction where, under drying, cross-linking occurs and the glass transition temperature is surpassed to enable a chemical change, and prevent any chance of water washing-off the stripe once coated. The following design specification for the product ink was employed, with a physicochemical rationale provided.

Design Specification:

Main formulation requirements:

- Thick solution (so that pigment does not fall out) – requiring cellulose or polymer materials.
- Stabilized solution (so flocculation only occurs "minimally") – requiring good surfactants and dispersing agents.
- No foam – requiring a defoamer (since the surface tension of water very high).
- Pigment "bound" to solution, electrostatic interactions of pigment with surroundings – this is important since the zeta potential of the pigment changes with pH.
- No cracking in the stripe (need correct level of binder).
- Small degree of solvent burn of the board (may need magnets to help this) or swelling of the board.
- No picking in the stripe (need correct degree of drying).
- Good resin system:
    - Emulsion (conventional evaporation),
    - Condensation reaction (chemical curing), or
    - Good drying technology:
        - IR (as already employed, may need to change wavelength of lamps).
        - For emulsion-based systems, co-solvent such as ethanol azeotrope may work.

- Main Challenges to overcome:
    - Dispersion in water (reduced flocculation/precipitation).
    - Foaming of the system under milling (surface tension of water is the highest of all common liquids).
    - Pigment binding to the substrate (water ingress/swelling).
    - Compatibility of the resin with the pigment.

- Drying times/evaporation kinetics.

The basic proposed emulsion formulation is given below in Table 7.9. This represents a template for the formulation and a description of the role of each component.

Table 7.9: Water-based emulsion formulation.

Material	Description
Water	Carrier
Natrosol 250 HR	Hydroxyethylcellulose non-ionic water-soluble polymer.
Rhodafac RE-610/E	Anionic surfactant
Dispex A40	Zwitterionic surfactant
BYK-024	VOC-free defoamer for aqueous systems
Dispex AA 4040	Dispersing agent for inorganic materials
Magnetite MO4232	Black magnetic pigment 4.0 – 6.0
Maghemite MO2228	Brown magnetic pigment – pH 3.0 – 5.0
Revacryl R245	Styrene acrylic copolymer, high pigment binding characteristics.
Primal Eco-15R	Self-cross-linking polymer resin

The basic condensation reaction formulation and corresponding resin solution is given below in Tables 7.10 and 7.11. This represents a template for the formulation and a description of the role of each component.

Table 7.10: Water-based chemical condensation formulation.

Material	Description
Water	Carrier
BYK-024	VOC-free defoamer for aqueous-based systems
Disper-BYK 193	Wetting/dispersing agent for aqueous printing inks
Magnetite MO4232	Black magnetic pigment 4.0 – 6.0
Maghemite MO2228	Brown magnetic pigment – pH 3.0 – 5.0
WBS-01	Resin solution
Alumina E330	Head cleaner
Prisorine 3505	Mild liquid fatty acid
Glyoxal	Dialdehyde compound

Table 7.11: Water-based chemical condensation resin solution.

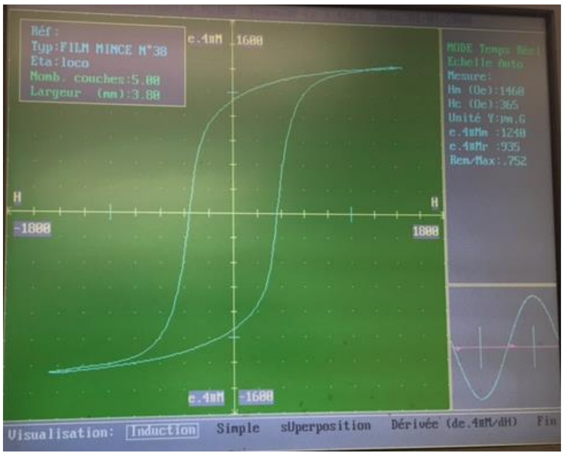
Material	Description
Hot water	Carrier
BYK-024	VOC-free defoamer for aqueous-based systems
Selvol E15/85	Water soluble PVA binder.

Several variations were attempted on the ‘emulsion’ formulation as above, with changes in surfactant types and chemical composition levels. Within these formulations, a water-based ink sample with magnetic functionality has been achieved. The characterization results of which are below in Table 7.12 and figures 7.14 and 7.15.

Table 7.12: Emulsion formulation Mini Attritor results.

Sample	Avg Solid Content %	Viscosity (cP)	SQ	SFD	Coercivity (Oe)
1	37.68	1507.398	0.777	0.606	364
2	36.89	1475.709	0.754	0.605	364
3	36.36	1454.386	0.762	0.619	363
4	37.61	1504.381	0.752	0.647	365
5	37.04	1481.44	0.759	0.542	365

Figure 7.14: Emulsion water-based ink formulation made on HMI mini attritor.



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Réf :
Typ:FILM MINCE N°38
Eta:loco
Nomb. couches:5.00
Largeur  (mm):3.00
```

```
MODE Temps Réel
Echelle Auto
Mesure:
Hm (Oe):1460
Hc (Oe):365
Unité Y:µm.G
e.4πMm :1240
e.4πMr :935
Rem/Max:.752
```

Figure 7.15: BH Looper analysis of HMI water-based sample.

The above figures show a sample that adheres to the required magnetic characteristics and is of expected texture upon dispensing from the attritor.

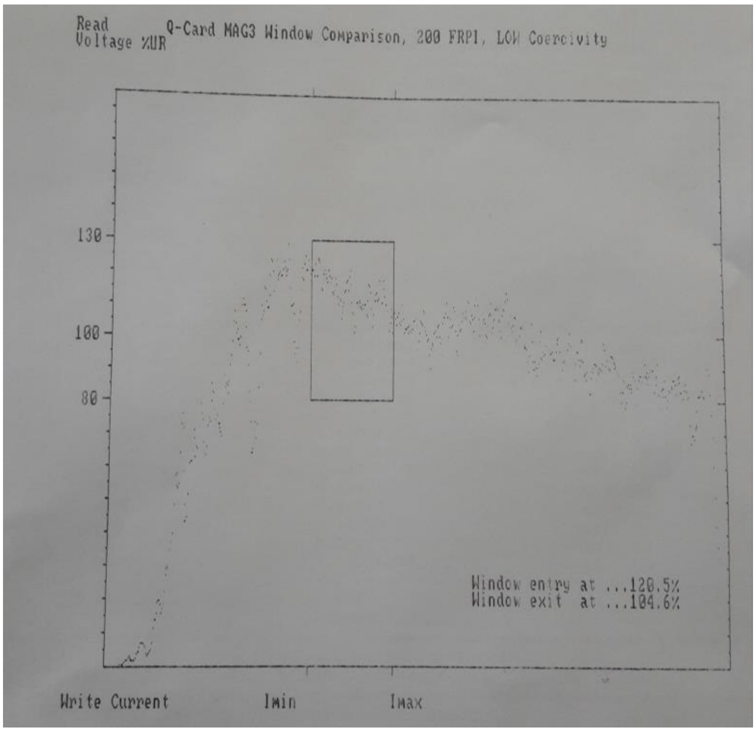
Unfortunately, after a period of only 24 hours the true instability of the formulation is represented in the sample tin, as flocculation and phase separation is observed. An example of this is shown in figure 7.16.

Figure 7.16: Instability in emulsion formulation after just 24 hours.

The observed instability can be improved through the use of appropriate wetting and dispersing agents but will require many more iterations to find appropriate components and levels.

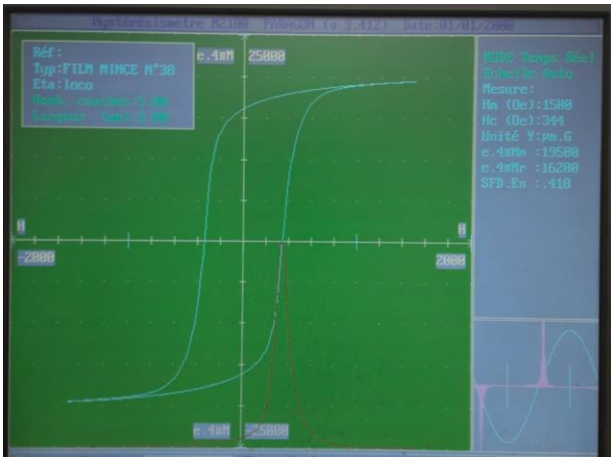
The 'condensation' formulation was also completed on the mini attritor. The initial formulation results and stability are depicted in figures 7.17 – 7.20.

Figure 7.17: Optical microscope image of the mini attritor condensation formulation.



```
Window entry at ...120.5%
Window exit  at ...104.6%
```

Figure 7.18: Mag3 results of the mini attritor condensation formulation.



```
Hystérésismètre M2100  PARAGON (v 3.412)  Date:01/01/2000

Réf:
Typ:FILM MINCE N°38
Eta:Ioco
Nomb. couches:5.00
Largeur (mm):1.00

MODE Temps Réel
Echelle Auto
Mesure:
Hm (Oe):1500
Hc (Oe):344
Unité Y:µm.G
e.4πMm :19500
e.4πMr :16200
SFD.En :.410
```

Figure 7.19: BH looper results of the mini attritor condensation formulation.

Figure 7.20: Condensation formulation on mini attritor.

Owing to the condensation route affording a stable formulation and excellent compliance to the proposed specification, the decision was taken to scale up the condensation formulation in the following two guises.

Two formulations were manufactured at production scale and coated onto TB2165 substrate using the Hull Magnacoater. The formulations were manufactured at a 30s scale, and quality assurance tested before being trialled in the coating room.

The first formulation, CR0001, was the condensation reaction formulation, but with the reaction components (Prisorine and Glyoxal) missing. This was to check formulation stability with and without the inclusion of these components, and show the effect of the condensation reaction on the final product. The second was the CR0101 formulation, to analyse the true effect of the condensation reaction components.

The first coating trial using formulation CR0001, was processed under various settings including variable coater speed and drying heat, but at a constant viscosity of 5500 cP. The product was completely dry and within specification at 20 m/min coating speed, and a heat intensity setting of 5. In turning up the speed and heat intensity, the maximum speed of normal production with VOCs (60 m/min) was reached, however the coat weight had to be lowered to allow full drying of the magnetic stripe. Figure 7.21 provides the magnetic characteristics of this product; figure 7.22 shows a photograph of the dried coated stripe made at 20 m/min and figure 7.23 the electromagnetic levels in the coating process.

Réf :
Typ:FILM MINCE N°38
Eta:loco
Nomb. couches:4.00
Largeur (mm):3.80

MODE Temps Réel
Echelle Auto
Mesure:
Hm (Oe):1530
Hc (Oe):324
Unité Y:μm.G
e.4πMm :9010
e.4πMr :7140
SFD.En :.405

Figure 7.21: CR0001 BH Looper results.

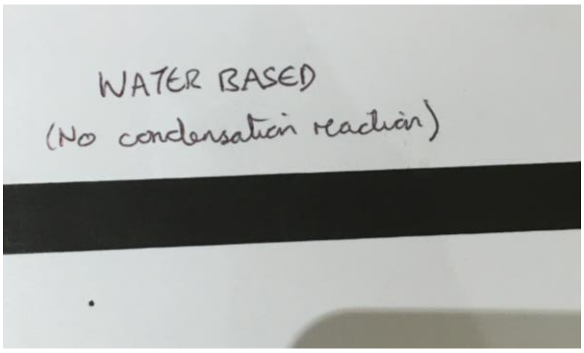


Figure 7.22: CR0001 Stripe produced on the Magnacoater.

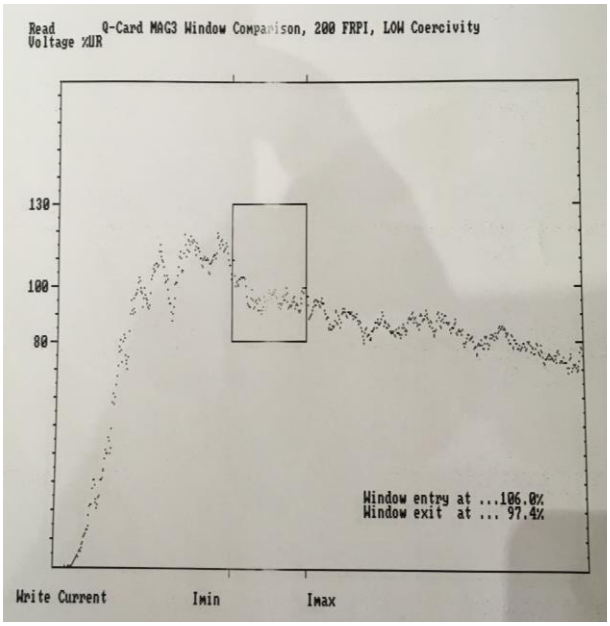


Figure 7.23: CR0001 Mag3 Results.

Following this, the CR0101 formulation was immediately coated. Unfortunately, it was not possible to fully and correctly dry the formulation before rewind due to the short 5 m drying bed on the Magnacoater. This may be due to the formulation naturally containing a higher water content, and the condensation reaction forming additional water during drying. There was also some ‘cracking’ in the magnetic stripes which may have been enhanced by the inclusion of the other components reducing the uniformity of the dispersion. Although the formulation did not produce any in-specification coated product to test, it did allow the effect of the condensation reaction to be tested.

To validate the theory, both dried CR0001 and CR0101 magnetic stripes were splashed with water to see if the stripe would ‘wash away’. The CR0001 stripe washed away with ease, however the CR0101 stripe was difficult to remove with water, proving the concept of the reaction within the formulation. The next steps for this development to be realised is to integrate the condensation components into the CR0001 formulation and reduce the water content within. It would also help to extend the drying capability of the Magnacoater, allowing for a longer drying period at a slightly reduced heat so that the stripe could be thoroughly dried. This combination of factors has real potential to produce a final ticket that could be launched to market.

In summary, a competitor benchmarking sample was obtained in the form of Pyral water-based low coercivity magnetic ink. This was characterized and passed all of the HMI quality assurance tests along with being a stable formulation. This demonstrated that a water-based ink is possible in HMI.

Two formulation routes were devised for the production of mAquetic ink in Hull. The emulsion and condensation-based systems were produced in several iterations in the lab. The emulsion formulation however was unstable after just 24 hours, but the condensation formulation produced much more promising results at a lab scale. The resulting decision was to scale up to production and coat the condensation formulation in a manufacturing trial. The formulation was coated with and without the inclusion of the chemical components forming the condensation reaction, however with the condensation components present, due to the generation of additional water it was not possible to completely dry the stripe at any speed. The formulation without the components showed excellent promise, and so the next steps are to return to small scale R&D to integrate these condensation components so that they can be used for a second trial. To make the project a success, some investment would be required to modify the drying system on the Magnacoater to allow scope for full drying of the water-based product.

In the next section, evaporation studies are studied to aid the identification of drying times for ink formulations, whilst providing a quality control tool for correct manufacturing.

7.4 Evaporation Rate Measurement as a Quality Control Tool for Quality Assurance for the Manufacture of Magnetic Inks Suitable for High Speed (60m/min) Printing

In any manufacturing environment, it is always important to be able to embrace a culture of traceability of any non-conformed product. For the case of ink manufacture, operator confusion, leading to mixing up solvents, or connecting the incorrect solvent drum to the solvent lines, can lead to disastrous consequences that are not trivial for a QA/QC team to unravel. Accordingly, simple methods for assessing whether the correct solvents were added in the correct ratios to products overcomes this QA/QC requirement. We chose to employ evaporation rate measurement to undertake this task, as such measurements would also impact through reassuring operators as to whether “picking” of the coated boards would take place during windings. Accordingly, this section first examines the theory underpinning evaporation rate measurement, followed by comparison of experiment with theory.

Theory:

We consider the evaporation of a liquid from a circular disc into a gas environment, limited by diffusive transport within the gas phase. We further assume that there is no evaporative cooling of the liquid surface that leads to a reduction of the vapour pressure [2]. Thus, in cylindrical space, the time dependence of the evaporation flux (j) within an axiosymmetric environment is given by Fick’s second law:

$$\frac{\partial c}{\partial t} = D\left\{\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right\} \qquad \text{Eq. 7.2}$$

where c is the concentration of the diffusing vapour at spatial co-ordinates (r,z) corresponding to the tangential and normal directions to the disc surface. The pertinent boundary conditions are as follows, assuming the atmosphere is solvent-free, and that the liquid | gas equilibrium is established rapidly at the interface.

Initial conditions: t ≤ 0 $c = 0 \quad \forall\ r, z$ (No solvent loss)

Temporal conditions: t > 0 $c = c^{eqm} \quad r \le r_0, z = 0$ (Interface)

$\frac{\partial c}{\partial z} = 0 \quad r > r_0, z = 0$ (Insulation boundary)

$\frac{\partial c}{\partial r} = 0 \quad r = 0, \forall\ z$ (Symmetry axis)

$c = 0 \quad r \to \infty, z \to \infty$ (Semi-infinite boundary)

In order to solve Equation 7.2, the following dimensionless variables are introduced [3].

Concentration: $$a = \frac{c}{c^{eqm}}$$

Time: $$\tau = \frac{4Dt}{r_0^2}$$

Space: $$R = \frac{r}{r_0};\ Z = \frac{z}{r_0};\ R = \sqrt{1 - \Theta^2}\sec\left(\frac{\pi}{2}\Gamma\right);\ Z = \Theta\tan\left(\frac{\pi}{2}\Gamma\right)$$

This enables Equation 7.2 to be transformed into Equation 7.3:

$$\frac{\partial a}{\partial t} = \frac{1}{4\left[\Theta^2 + \tan^2\left(\frac{\pi}{2}\Gamma\right)\right]}\left\{\frac{4}{\pi^2}\cos^2\left(\frac{\pi}{2}\Gamma\right)\frac{\partial^2 a}{\partial \Gamma^2} + \left(1 - \Theta^2\right)\frac{\partial^2 a}{\partial \Theta^2} - 2\Theta\frac{\partial a}{\partial \Theta}\right\}$$

Eq. 7.3

This “trick” in moving from cylindrical polar co-ordinates to conformal space overcomes the issue of infinite flux at the mathematical singularity (at the rim of the liquid disc), and enables accurate and fast solution using the method of finite differences, exploiting the alternating direction implicit method to solve in two-dimensional spatial co-ordinates. Note that in quasi-conformal space, Θ = 0 corresponds to the insulation plane; Θ = 1 corresponds to the symmetry axis and Γ = 1 refers to the semi-infinite limit. We are interested in the evaporation rate, $-\frac{dm}{dt}$, which describes the rate at which mass is lost through evaporation at the interface. This is given as:

$$-\frac{dm}{dt} = 2\pi MDc^{eqm} r_0 \int_0^1 \left(\frac{\partial a}{\partial Z}\right)_{Z=0} R\,dR = 4MDc^{eqm} r_0 \int_{\Theta=0}^{\Theta=1} \left(\frac{\partial a}{\partial \Gamma}\right)_{\Gamma=0} d\Theta \qquad \text{Eq. 7.4}$$

where M is the molar mass of the volatile species. Thus, the normalised evaporation rate, e, is given by:

$$e = \frac{-\left(\frac{dm}{dt}\right)}{4MDc^{eqm} r_0} = \int_{\Theta=0}^{\Theta=1} \left(\frac{\partial a}{\partial \Gamma}\right)_{\Gamma=0} d\Theta \qquad \text{Eq. 7.5}$$

so that the evaporation rate at steady state is given by e = 1, or equivalently,

$$-\left(\frac{dm}{dt}\right)_{t\to\infty} = 4MDc^{eqm} r_0 \qquad \text{Eq. 7.6}$$

Equation 7.6 is referred to as the Ward Equation, and demonstrates that provided measurements can be made at steady state, the evaporation rate is a function of both the nature of the solvent (from the molar mass) and its concentration in the liquid phase, since, assuming the gas phase system behaves perfectly, and the liquid phase system behaves ideally,

$$c^{eqm} = \frac{xP^*}{RT} \qquad \text{Eq. 7.7}$$

where R is the molar gas constant (8.3145 J mol^{-1} K^{-1}), T is the absolute temperature, P^* is the vapour pressure of the pure solvent and x is the mole fraction of the solvent in the liquid. This steady-state measurement therefore empowers the QA/QC functionality as envisaged above.

In order to determine the temporal dependence of the evaporation rate, Equation 7.3 was solved using an expanding temporal grid developed by Amatore [4], *viz.* for a very short times ($\tau \leq 0.025$), the time difference was kept uniform at $d\tau_0 = 2 \times 10^{-4}$; above this time, the time difference varied as $\Delta t = (1+\omega)^{k-k_0} \Delta t_0$, where k refers to the number of time steps, k_0 is the number of time steps for which the temporal grid is uniform, and w is the temporal grid expansion factor. Simulations were undertaken in Matlab (version R2013a), using a 100 x 100 spatial grid, with w = 5 x 10^{-5} (see Appendix 10 for a copy of the script file used).

Simulations required 715 s of computing time, when executed on a MacBook Air laptop equipped with a 1.3 GHz Intel Core i5 process and 4 GB RAM.

Figure 7.24 illustrates the temporal variation of the evaporation rate. The small oscillations at short time periods correspond to the short-time instability of the alternating direction implicit method. These data conform to the following general expression for transient-to-steady state transitions at disc surfaces, first developed by Shoup and Szabo [5], which is accurate over all time to 0.6%:

$$e=\frac{-\left(\frac{dm}{dt}\right)}{4MDr_0c^{eqm}}=0.7854+\frac{1}{2}\sqrt{\frac{p}{t}}+0.2146\exp\left(-\frac{0.3192}{\sqrt{t/4}}\right) \quad \text{Eq. 7.8}$$

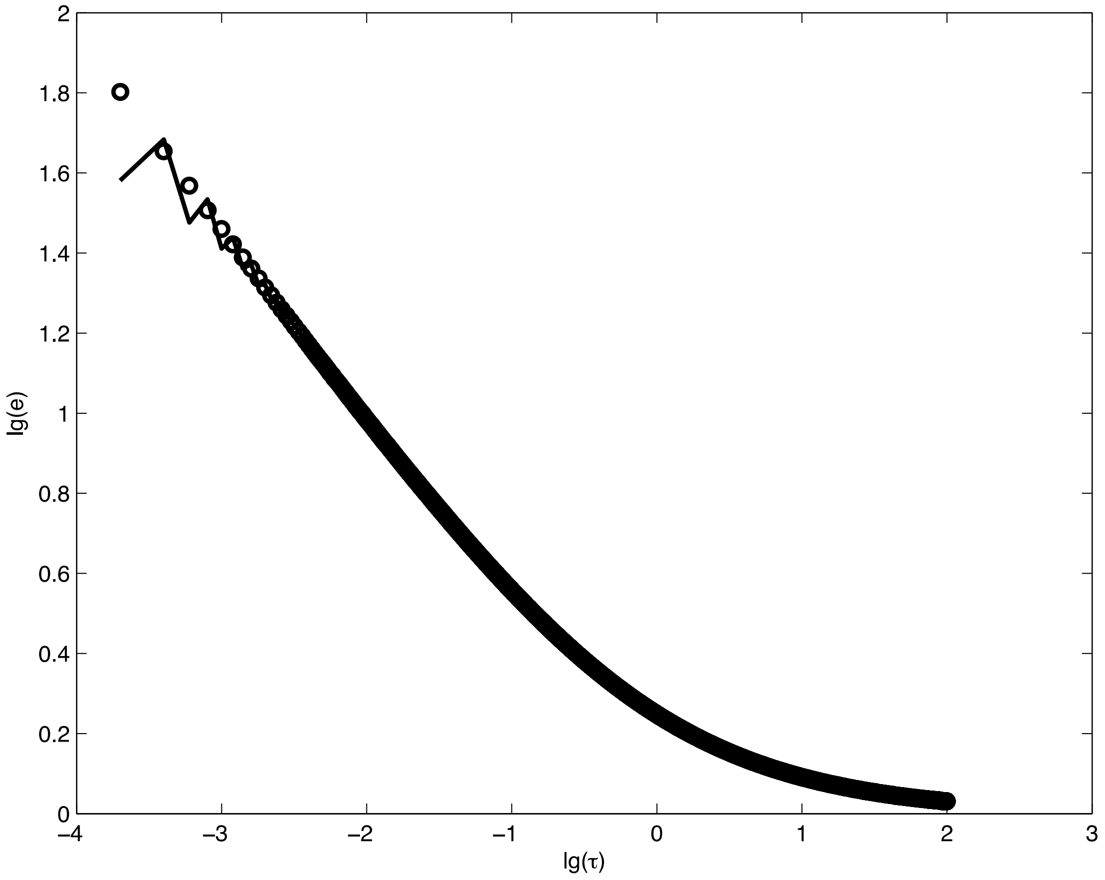


Figure 7.24: Plot of simulated evaporation rate with dimensionless time. Solid line corresponds to the finite difference simulation; the open circles correspond to the analytical approximation given in Equation 7.8.

Having established the theoretical fundamentals underpinning this measurement, we next seek to examine its robustness with a variety of solvents and slurries used or manufactured at HMI.

Experimental:

A modified Stefan tube was fabricated from PTFE. In this version, a 5.4 cm diameter cylinder (of length 5.4 cm) was machined from PTFE, with a 2 mm diameter hole cored centrally, to a depth of around 4.8 cm, to form a cylindrical pot. The liquid or ink slurry to be tested was filled into this pot and the surface scraped with a sheet of PET, such that the liquid surface was flush with the upper level of the insulation. This allowed for the liquid level to be flush with the top part of the insulation. The width of the insulation (1.7 cm wide around the circumference of the liquid) enabled a mathematically well-defined system to be experimentally realised, with diffusion of liquid being enabled in directions both normal and tangential to the liquid disc surface. The thick insulation ensured that no back diffusion would take place, enabling a simplification of the system. The particular dimensions chosen were aimed to minimise the time required for the occurrence of steady-state measurements. Steady-state behaviour is observed whenever the diffusion layer corresponding to the loss of solvent from the liquid disc becomes larger than the characteristic dimension of the liquid disc, *viz.*, the solution to the equality:

$$\frac{pr_0}{4} = \sqrt{pDt} \tag{Eq. 7.9}$$

where r_0 is the radius of the liquid disc (1 cm), D is the solvent diffusion coefficient in the gas phase (typically between 1-10 cm^2 s^{-1}) and t is the time taken to reach steady-state. For the system to approach steady state rapidly ($2 \leq t/s \leq 20$), r_0 needs to be typically around 1 cm. The advantage of this approach compared with conventional Stefan tubes is that there is no need to flow gas at some distance away from the surface to impose a Neumann boundary condition, since this is naturally imposed at semi-infinite distances from the disc surface. This simplifies and reduces the cost of the experimental equipment, enabling measurement to be undertaken by operators.

Measurements were undertaken in a well-ventilated environment that had not been previously exposed to the solvent, at ambient temperature (23 ± 2 ^{o}C). For the case when the solvent was water, the relative humidity was measured as being between 50-70%. Measurements were recorded as the total mass of the pot (filled with liquid), using an analytical balance correct to four decimal places.

Interpretation:

We first consider experimental data corresponding to pure solvents. Figure 7.25 presents the mass-time data recorded when IPAC is the solvent, which clearly indicates the loss in mass due to solvent evaporation over time. It is apparent that the rate at which the mass is lost changes with time, initially decreasing to a steady value.

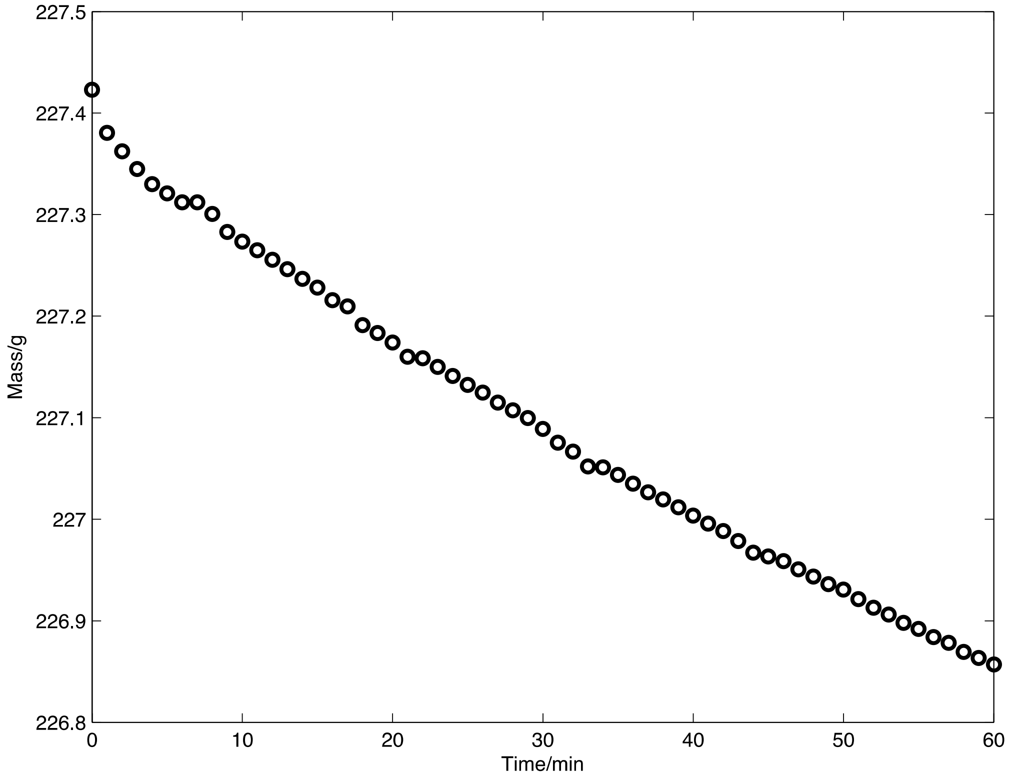


Figure 7.25: Mass-time curve for the evaporation of IPAC.

In order to extract the evaporation rate, the data in Figure 7.25 were differentiated with respect to time, and replotted (see Figure 7.26), where it is seen that in the steady-state limit, the experimental data conform to that theoretically expected, using the data in Table 7.13, and the Ward equation (Equation 7.6).

Table 7.13: Physical constants of several solvents employed at HMI for the manufacture of inks.[a]

Solvent	Molar Mass /g mol^{-1}	Density /kg m^{-3}	Gas Phase Diffusion Coefficient /10^{-2} cm^2 s^{-1}	Vapour Pressure of the Pure Liquid /kPa
Water	18	997	24.2	3.17
Methyl ethyl ketone	72.11	805	13.3	12.6
Isopropyl acetate	102.13	870	12.4	5.60

[a]Data obtained from CRC Handbook for Chemistry and Physics, reference [6], for temperatures of 298 K.

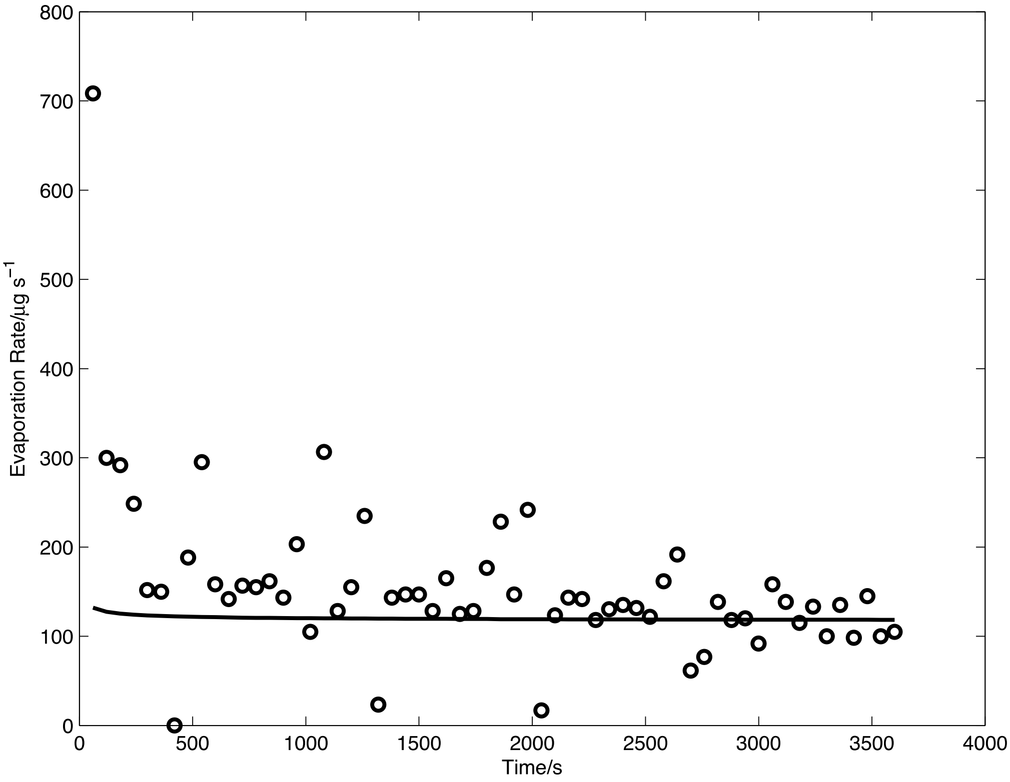


Figure 7.26: Temporal dependence of the evaporation rate for IPAC. Circles represent the experimental data extracted from Figure 7.25; the solid line is computed from Equation 7.8.

It is clear that there is very good agreement between experiment and theory: the expected loss is 115 µg s^{-1}; the observed loss is 123 ± 31 µg s^{-1}. Similar agreement was observed for the case of MEK (see Figure 7.27). However, the observed loss of 142 ± 22 µg s^{-1} is smaller than that anticipated at steady state, 195 µg s^{-1}. This discrepancy is rationalised through the fact that MEK is more volatile than IPAC, so that the faster evaporation rate leads to a great degree of cooling of the surface, coupled with the development of "recessed" disc, *viz.*, the level of the liquid in the cylindrical pot falls below the level of the insulation.

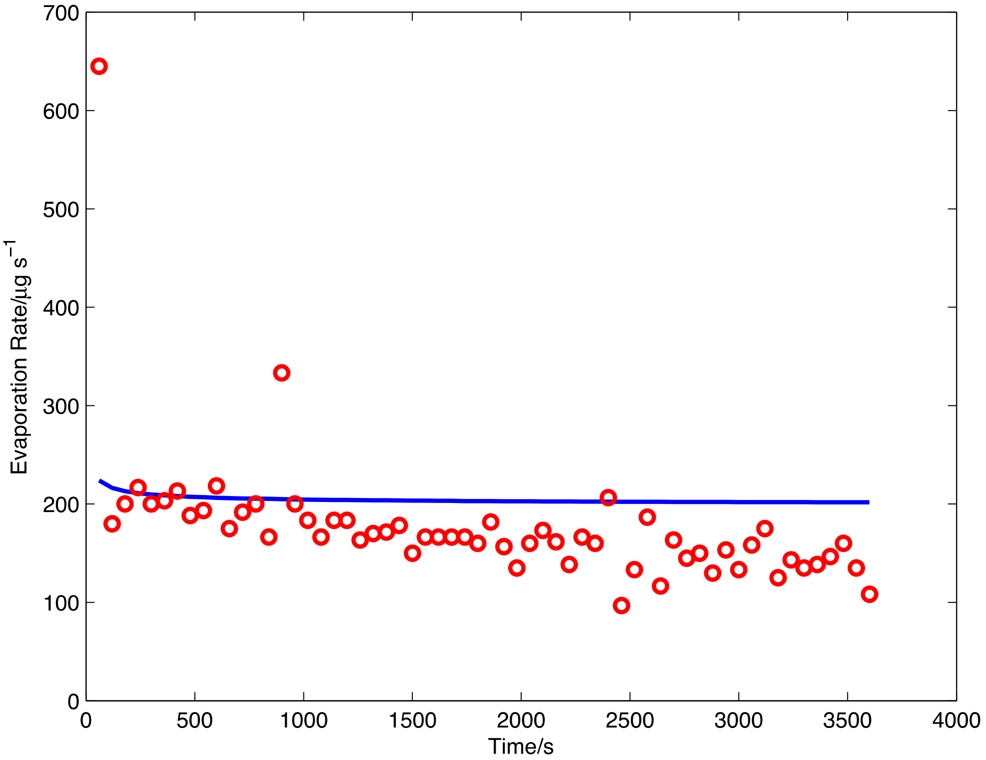


Figure 7.27: Temporal variation of the evaporation rate for pure MEK. Red circles correspond to experimental data; the blue line was calculated using Equation 7.8 and the data in Table 7.13.

Next, we consider the evaporation rates from two magnetic inks: a recently manufactured sample of HL0104 (corresponding to French motorway ink) and an old sample (manufactured in December, 2014, but examined in May, 2016) of FHL0201 (used by RATP on the Paris Métropolitain). In these inks, two solvents are used: IPAC at a mole fraction of 0.672 and MEK at a mole fraction of 0.067. Accordingly, using the Ward equation (Equation 7.6), we expect a steady-state evaporation rate given as the summation of the mole fraction weighted evaporation rates of the individual solvents, *viz.*,

$$e = \frac{4r_0}{RT}\left(M_1 D_1 x_1 P_1^* + M_2 D_2 x_2 P_2^*\right)$$

Eq. 7.10

Using the data in Table 7.13, Equation 7.10 yields an expected evaporation rate of 91.6 μg s^{-1} in both HL0104 and FHL0201 (as they have the same mole fraction of the mixed solvent). Figure 7.28 demonstrates that the experimental data for the evaporation of HL0104 afford an evaporation rate of 71.0 ± 16.1 μg s^{-1} at steady-state, which is in approximate agreement with that expected from theory, suggesting that the batch of HL0104 examined by this method appears to have been manufactured in the correct way.

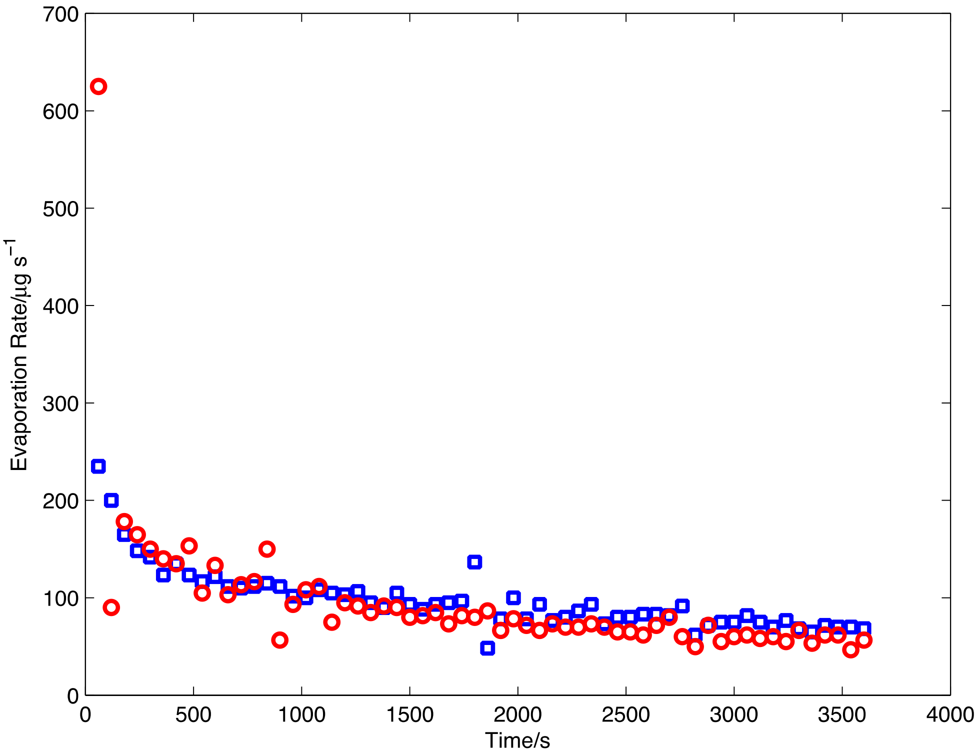


Figure 7.28: Evaporation rate change for the batch of HL0104 tested. Two experimental runs are shown: the first run correspond to the blue squares; the second run is illustrated by the red circles.

For the case of the old batch of FHL0201, the experimental data afford an evaporation rate of 53.0 ± 12.8 μg s^{-1} at steady-state (see Figure 7.29). This is almost half the expected value, and serves to identify this batch of old magnetic ink as being unsuitable for use in sale to customer.

Interestingly, the transient shape for evaporation in the magnetic inks is significantly different from those seen in the case of the pure liquids (Figures 7.26 and 7.27) where the experimental data are essentially at steady-state at all times measured. For the magnetic inks (Figures 7.28 and 7.29), we propose that the shape arises owing to a breakdown in the assumptions of the model: with the magnetic inks, the transport of the solvent from deep within the pot to the interface may start to play a rôle before steady-state is fully established.

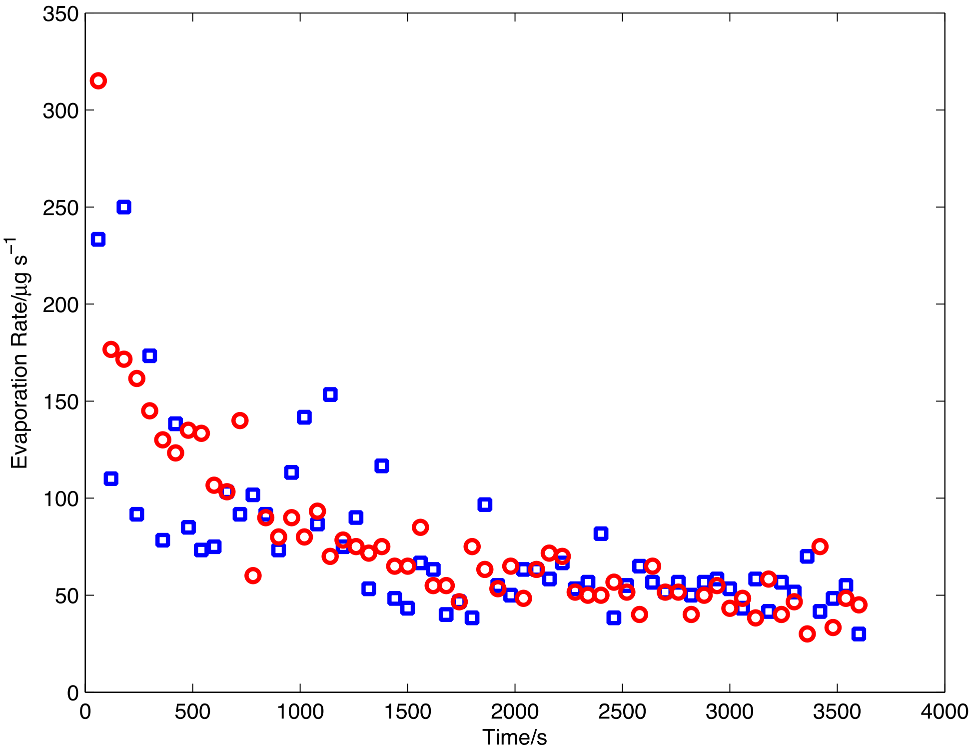


Figure 7.29: Evaporation rate change for the batch of FHL0201 tested (Batch 13, December manufacturing). Two experimental runs are shown: the first run correspond to the blue squares; the second run is illustrated by the red circles.

In summary, a low-cost solution to verify whether a particular magnetic ink has been manufactured correctly, has been presented through evaporation rate measurements. This experiment is simple, easy to perform, rapid and requires minimal data analysis, enabling it to be performed at operator level. The incorporation of this type of methodology into the manufacturing enables confidence in the rigour of the QC/QA testing.

Having innovated in the development of magnetic inks and their processing, the next chapter investigates the use of magnetic tickets for covert threat detection.

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Chapter 8 - Project ITUS

This chapter is concerned with the invention of a rapid and on-site identification of explosive material that may be present on the surface of a ticket used in public transportation. It utilizes an electrochemical method of detection, and capitalizes on the fact that when tickets (such as train tickets, certain bus tickets, *etc.*) are verified so as to open a barrier, the ticket-holder is separated from the ticket, as the latter passes through a verification machine. During this process, whilst the coding (bar code, magnetic stripe, magnetic numbers, *etc*.) on the ticket is being checked, it is possible to utilize fast and low-cost analytical measurements to determine whether there are additionally any residues of explosive matter, or even precursors to explosive matter, present on either side of the ticket. This form of chemical reconnaissance empowers a route through which evidence may be gathered covertly, in advance of a potential targeted terror attack, or in assisting the tracking and tracing of potential "get-a-ways." It may act in the capacity of the proactive and discrete security surveillance of passengers, thereby potentially enabling the safety of innocent bystanders, through the provision of a latent early-warning system for security services.

The development of analytical chemical methods and techniques for the security services holds a long and well-established history, as these may afford early preventative measures for terror attacks in spaces where the public may be confined (such as underground transport networks, busses, within airports, *etc.*) [1]. A number of companies and researchers have focused efforts on developing systems for these purposes, including for ticketing machines [2-5]. However, these utilize expensive equipment that is difficult to miniaturize, such as gas/ion chromatography apparatus coupled with mass spectrometry detection. These systems provide information pertaining to the molecules being detected and are reasonably sensitive to residues under laboratory testing conditions. In the field, however, the sensitivity is related to the instrument size, and, more importantly for *reconnaissance*, are not easy to disguise – the speed of monitoring needs to be at least as fast as the timescale for ticket validation, without any loss in sensitivity. It is for these reasons that electrochemical sensing of explosives is an important and innovative route through which powerful analytical performance (low sensitivity on the order of zepto-to-nano-moles of analyte) and fast (as low as nanosecond measurements) quantitative information may be provided, from miniaturized and low-cost instrumentation [6,7].

Many modern explosive materials are organic compounds containing functional groups which include constrained species with weak bonds such as N-N, O-O, nitroaromatics or nitrosoaromatics or nitramines [8]. These functional groups are electrochemically active and their quantitative presence is readily ascertainable through their characteristic signatures in the voltammetric current-voltage plane. Voltammetry is the technique in which the potential of a working electrode *versus* a reference electrode follows a time-dependent function, and the current flowing between the working electrode and a counter electrode is monitored. The potential excursion may comprise a step, pulse, ramp perturbation, or a combination of these. The reference electrode and the counter electrode may comprise two distinct electrodes, or a single combined electrode, depending on the particular requirements of the operating system. The working electrode may be of macroscopic (millimetric) or microscopic (micrometric or nanometric) characteristic length (such as diameter for disc electrodes, length for band electrodes, *etc.*). A voltammetric sensor operates through fingerprinting a characteristic potential (such as a peak potential in transient conditions, or half-wave potential if the system operates under steady-state conditions) corresponding to the confluence between electrode kinetics and material transport for the case of a freely diffusible entity (or due to electrode kinetics and material exhaustion for the case of material present within a thin layer close to the electrode) along the potential scale. Peak potentials may be positive (corresponding to an oxidative process) or negative (corresponding to a reductive process), in the standard IUPAC convention, and pertain to the maximum (or minimum) current flowing associated with the Faradaic process of interest. A half-wave potential is the potential that corresponds to half of the steady-state current. The problem that often faces voltammetric sensors in real-life practical conditions is that the reference electrode may drift over time. This is readily guarded through adopting internal calibration (wherein a particular compound, such as the IUPAC conventional internal standard, is present), so that all potentials can be corrected in reference with the characteristic potential of this standard material. This then empowers the knowledge of the identity of the redox signatures observed, with the value of the current that flows being a quantitative guide to the functional groups that may be present.

In this chapter, we propose the use of a ferrocene derivative as an internal standard that is present on the *recto* and *verso* sides of a transportation ticket. It may be present in a varnish coating over the whole ticket, or in merely within a single part of a ticket (such as being contained within the magnetic stripe on the *verso* side of an underground rail ticket). The varnish that may be used by the ticket may be of an electrically conductive (such as that imposed by varnished comprised of conducting polymers or ionic liquids), semi-conductive or insulating nature. As the method described herein requires the passage of electricity, varnishes that do not have sufficient electrical conductivity require the use of a conductive electrolyte solution through which the electrodes may contact the surface of the ticket; those varnishes that are of sufficiently high conductivity will enable interfacial charge flow to take place when the electrodes contact the surface of the ticket, and under these circumstances, it is important to ensure that a short-circuiting of the electrodes does not happen.

The concept underpinning the measurements made in this chapter is illustrated within the cartoon exhibited in Figure 8.1, wherein it is readily observed that the system requires contact of electrodes with ticket. For the monitoring of both *recto* and *verso* sides, two sets of electrodes are required. Depending on the route through which the system may be made to work in the field, multiple sets of electrodes may be required on both ticket faces, so that in the case where the ticket varnish is electrically insulating, the full ticket may be monitored. In the manifestation of the invention depicted in Figure 8.1, the electrode probes comprise two working electrodes, one reference electrode and one counter electrode. In this arrangement, as the ticket passes through the electrochemical reader, one of the working electrodes is biased towards oxidative potentials, with the other working electrode biased towards reductive potentials, both *versus* the reference electrode, with the current observed between each of the working electrodes and the counter electrode. The exact form of the potential perturbation may comprise a conventional voltammetric waveform, such as that employed by linear sweep voltammetry, cyclic voltammetry, or a pulse voltammetry (for example differential pulse voltammetry, normal pulse voltammetry or square wave voltammetry). It is imperative that the timescale of the perturbation is very much smaller than the timescale for the ticket card passing, so that reading along the ticket card is achieved. This holds a knock-on effect for the size of electrodes used, as this affects the time constant of the cell [7]. The purpose of the dual biasing of the working electrodes is so that one electrode covers the internal standard and the other monitors any explosive compound residues that may exist on the side of the ticket being investigated. Since the functional groups present in explosive materials are more readily reduced than oxidized, having an internal standard in a different quadrant of the voltammetric plane enables the ready distinction between potential explosive analyte and internal standard.

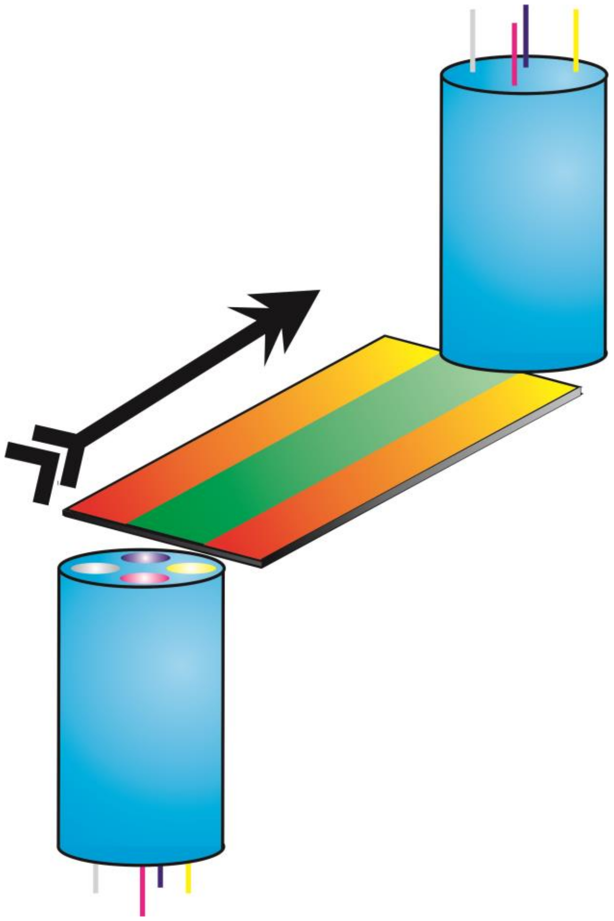

Figure 8.1: Cartoon illustrating the principle underpinning the present invention. A transportation ticket is read on both recto *and* verso *sides by an electrochemical probe whilst the ticket is in the mass transit barrier. The leads from the probes are connected up to electrochemical instrumentation (not shown) that may have wireless or LAN connectivity capability. The arrow indicates the direction of travel. Note that in this manifestation of the invention, two working electrodes (one to read the internal standard and one to explore the ticket) are used with a counter electrode and a reference electrode.*

The internal standard itself may be chosen so that it may be exploited to act as a route through which the "track-and-trace" of the number of times the ticket has been read, may be inferred. In the case where the ticket varnish is electrically insulating and a jet of electrolyte solution is pumped over the ticket surface immediately prior to its reading, the internal standard, which has be to chosen such that it has extremely low solubility within the electrolyte (so as to prevent its dissolution during ticket handling in rainwater, or through palm sweat, or through saliva in the case where the ticket is licked), may be chosen so that it remains insoluble in the electrolyte *after* the relevant Faradaic process, or where the Faradaic process drives the dissolution of the redox-transformed internal standard into the electrolyte [9]. Since the current passed during the course of

Faradaic electrolysis empowers knowledge of the surface coverage of the electroactive species undergoing redox transformation, the magnitude of the current may be exploited, in the case of a Faradaic dissolution of the internal standard, to quantify the number of times the ticket has been previously read. Inasmuch as it is not normal for a disposable ticket to hold individually unique identifiers that are at present read during the course of barrier-opening, if it were to take place (for example through the use of electrochemically written codes), the resulting exquisite internet of explosive residue sensors may afford important "big data" for predictive analytics: the knowledge of the where the ticket has been previously read, on which ticket reading the presence of explosive residue occurs, allow counter-terrorist services to understand the movements and track the locations of potential terrorists or potential terrorist cells and their suppliers, thereby anticipating a stronger line of defence for innocent bystanders [10].

The work undertaken that demonstrates a proof-of-concept is next outlined. For simplicity and ease, whilst highlighting merely the electrochemical detection pathway, the only experiments undertaken incorporated an internal standard within the magnetic ink formulation that has been qualified for use on the Paris Métropolitain by RATP, with the rotogravure printing of this ink, and testing undertaken through contact of the electrodes with the printed surface. Two compounds were selected as models to mimic explosive residues. These materials were nitrobenzene (to mimic HNB, TNT, *etc.*) and *ortho*-nitrophenol (to mimic picric and styphinic acids). An exhaustive list was not considered within this proof-of-principle investigation. Likewise, in order to demonstrate the operation of the electrochemical sensing protocol, the printed substrate was not moved through the detector; rather it remained stationary during experimentation.

The magnetic ink was formulated as follows. The internal standard (either *tert*-butylferrocene or ferrocenecarboxylic acid) was made up to a concentration of between 2-10 mM in isopropyl acetate, using 10 mL of the solvent. This was poured into the stainless steel 8007 SPEX Sample Prep container holding five 0.5

inch hardened steel balls. The following compounds were added to the reaction vessel. 0.4 g Vinnol E 15/40 ATF (co-polymer of vinyl chloride and acrylic acid esters), 0.16 g Rhodafac RE/610 (surfactant), 0.104 g Metarin P E322 (soybean lecithin surfactant), 0.104 g E330 alumina (head cleaner), 0.104 g BYK070 (silicone and polymer based defoamer), 2.83 g magnetite (MO4232) and 8.48 g maghemite (MO2228). These materials were milled for 60 min within a 8000M SPEX Sample Prep Mixer/Mill to form a slurry that was let-down for 15 min within the mixer/mill with a pre-mixed resin comprising 10 mL isopropyl acetate, 1.6 mL methyl ethyl ketone, 2.64 g Vinnol E 15/40 ATF and 0.6 g diisononyl phthalate, to form the magnetic ink.

The magnetic ink was printed onto a polyester film using an RK Print K Printing Proofer equipped with a rotogravure printing head and a standard D plate. Magnetic characteristics of this ink, when orientated with a bespoke ~1200 G magnetic assembly attached to the proofer head, and measured with a BH looper (M2100 Hysteresis meter, S.I.I.S), revealed characteristics typical for the application in underground train tickets, *viz.* coercivity 335 ± 12 Oe; squareness >0.7; switching field distribution <0.7.

Electrochemical experiments were undertaken using an AUTOLAB PGSTAT30 bipotentiostat system (Eco Chemie, The Netherlands) in a three-electrode set up, employing a 3 mm diameter glassy carbon working electrode (BAS), nickel wire counter electrode and saturated calomel reference electrode (Radiometer). In order to mimic operating conditions, the counter electrode was wrapped around the reference electrode, and the working electrode held within a micromanipulator. These were positioned over part of the polyester that had been printed with magnetic ink, with an aliquot of aqueous 0.1 M potassium chloride electrolyte pipetted between the electrode ensemble and the printed surface. Preliminary experiments revealed that the distance between the working electrode and the printed ink enabled a control of the degree of oxidation of the ferrocene derivative within the ink. Accordingly, all subsequent experiments were undertaken with the whole electrode ensemble in contact with the printed surface, although the force applied to keep the working electrode in position was not measured. Although initial experiments were conducted using cyclic voltammetry so as to verify the feasibility of the concept, all subsequent experiments were undertaken using square-wave voltammetry, using a frequency of 25 Hz, amplitude of 20 mV and step of 2 mV, resulting in an experimental timescale of 0.5 s. The optimization of these parameters was not an objective of this preliminary proof-of-concept investigation. All experiments were undertaken under ambient conditions, corresponding to a temperature of 22 ± 2 ^{o}C.

Experiments to mimic the presence of explosive residues were undertaken through pipetting a small (10 µL) aliquot of a solution of either nitrobenzene or *ortho*-nitrophenol at a concentration of 2 mM in methyl ethyl ketone over the surface of the printed ink, and allowing the solvent to evaporate under ambient conditions. In this way the surface of the printed ink is modified with 20 nmol of nitrobenzene or *ortho*-nitrophenol. The formation of the random arrays of microdroplets or microparticles in this way empowers a mimicry of the random distribution of explosive residues on a surface through its handling [6,9,11,12]. The working electrode was then positioned over this modified surface and electrochemical experimentation performed as for the unmodified case.

Figure 8.2 illustrates typical square-wave voltammograms of the ferrocene derivative (RFc) printed on a polyester support. Note that these data have not been baseline-corrected. The oxidation of the ferrocene species is marked by the characteristic peak, which occurs at the formal potential, and corresponds to the electrochemically-induced dissolution of the ferricenium cation:

$$\mathrm{RFc(s)} - e^{-} \rightarrow \mathrm{RFc^{+}(aq)} \qquad \text{Eq 8.1}$$

For the case of ferrocenecarboxylic acid, this potential is observed to be at 0.2718 ± 0.0030 V *vs.* SCE; for the case of *tert*-butylferrocene, this peak occurs at 0.1638 ± 0.077 V *vs.* SCE. These values are in roughly in agreement with those anticipated from literature studies [11,12].

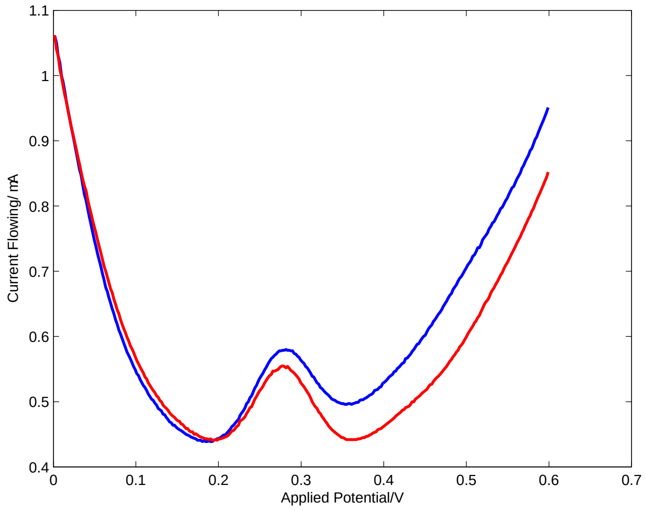

Figure 8.2: Square-wave voltammograms at a glassy carbon electrode corresponding to the oxidation of ferrocenecarboxylic acid embedded within printed magnetic ink, and in the presence of aqueous 0.1 M potassium chloride. The blue signal corresponds to the first "reading" of the printed matter; the red signal is the second reading.

Since the electrode was in contact with the printed surface, the voltammetry observed is that corresponding to thin-film behaviour, and thus the size of the signal (specifically the charge passed) is related to the amount of material present within the printed surface. Since the plates on the proofer vary in terms of cell depth, assuming the mixing process affords a uniform surface concentration of the ferrocene derivative, and that the amount of dried ink left on the polyester surface is proportional to the cell depth, the signal observed should increase with cell depth. This was found to be the case: cells of depth 40 µm afforded peak currents that were four times larger than those of 36 µm depth. Likewise, owing to the electrolysis corresponding to irreversible material consumption from the printed surface, the extent of dissolution is from repeat measurements at a particular site was observed to depend on the thickness of the printed surface: approximately *ca.* 16% loss was observed from surfaces printed with cells of 40 µm depth, with *ca.* 35% loss from those surfaces printed with cells of 38 µm depth. This is to be expected, and afford evidence of the feasibility of the "track-and-trace" approach claimed.

Figure 8.3 depicts the voltammetry of the reference ferrocene derivate in the presence of a model organic explosive compound. It is clear that the reference signal is observed even in the presence of the residue impurity. The modification of the surface in a random manner with this residue may elicit a change in the peak potential of the reference, owing to it covering the reference compound and thereby partially blocking the signal. Such effects typically manifest in an alteration of the electrode kinetics of the process, resulting in a potential shift and a reduction in peak current, associated with the lowering of the heterogeneous rate constant for the electrode reaction, coupled with a reduction in the peak height [7,13,14]. Inasmuch as this identifies the presence of material over the surface, it does not afford knowledge of its identity. This is one of the reasons why it is proposed that the full monitoring of both *recto* and *verso* surfaces of a ticket occurs. Also shown in Figure 8.3 is the voltammetry corresponding to the presence of the model explosive compound on the surface of the printed ink. It is clear that the signal that occurs is within the third quadrant of the voltammetry plane, occurring at potentials that do not interfere with the presence of the internal standard.

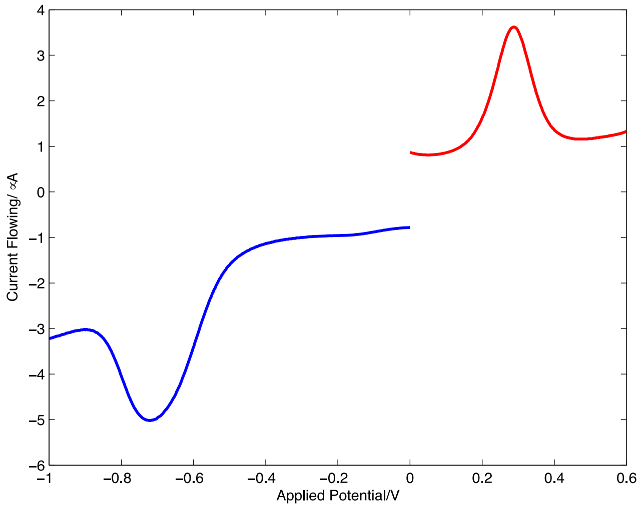

Figure 8.3: Square-wave voltammograms at a glassy carbon electrode corresponding to the oxidation of ferrocenecarboxylic acid embedded within printed magnetic ink (red signal), and of the reduction of ortho-nitrophenol (blue signal) present in the form of microparticles over the printed matter. The aqueous electrolyte was 0.1 M potassium chloride.

Aromatic nitro-groups typically follow a four-proton, four-electron pathway followed by a two-electron, two-proton electrochemical reduction in the presence of aqueous electrolyte. An extensive study of the mechanism of these processes has been undertaken by Wain and co-workers [15]. All other things being equal, the size of this electrochemical signal compared with that of the internal standard may enable the quantification of the amount of this functional group present on the surface. The difference between the peak potential observed for the reduction of the nitro-group and the oxidation of the ferrocene derivative serves to fingerprint the identity of the residue compound. In the case of ferrocenecarboxylic acid as the standard and *ortho*-nitrophenol as the residue, the peak potential difference was observed to be 1.0245 ± 0.0211 V; for the case of *tert*-butylferrocene as the standard and nitrobenzene as the residue, the peak potential difference was observed to be 0.9561 ± 0.0301 V. These differences are expected to change with the working electrode material, but, nevertheless, afford a proof-of-concept of the system.

In summary, this work has illustrated the deployment of an electrochemical sensing strategy for the detection of organic explosives in the presence of printed inks.

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Chapter 9 – Conclusion and Future Directions

The main objective of the KTP was to establish the Company's own manufacturing capability of magnetic inks to remove the reliance on current at-risk magnetic ink suppliers. Additional objectives were the introduction of ink formulations ridding volatile organic compounds, and finally the development of new formulation technologies for security applications.

The main objective was the installation of the HMI facility and the ability to manufacture four magnetic inks. Following success of formulation at a small scale, the HMI manufacturing area, QA and R&D laboratories were constructed. The room complied with the ATEX regulations outlined through DSEAR, ISO 9001:2015 and 14001:2015. A total of thirteen formulations have been developed and approved since the project start date, exceeding the initial project scope. This development took a total of three years, with the final HH0307 product being qualified in October, 2017. It can be concluded that this phase of the project has been an astounding success, leading to the Company developing new products for new markets in addition to securing their supply chain. The economic impact has been to triple the Company's turnover, which has led to the University/Industry Partnership being *highly commended* in the Commercial Engagement category of the 2016 Educate North Awards, *shortlisted* as the Knowledge Exchange/Transfer Initiative of the Year at the 2016 Times Higher Education Leadership & Management Awards, winning the *Turnaround Award* in the 2017 Yorkshire Post Excellence in Business Awards, and winning the *Investment Award* at the 2018 Yorkshire Business Masters. Furthermore, the candidate won in the Hull and Humber *Top 30 under 30 Awards*.

For the development of a water-based magnetic ink, there are several advantages aside from the reduction in VOC emissions, such as removing the need to maintain an ATEX rated process room and the opening of unique marketing opportunities. A stable and functional formulation has successfully been produced with an aqueous based carrier. The formulation incorporates a condensation reaction to provide a cross-linking mechanism that prevents solubility in water following curing of the ink. Further iterations are required to integrate this at a manufacturing scale along with a modified drying system.

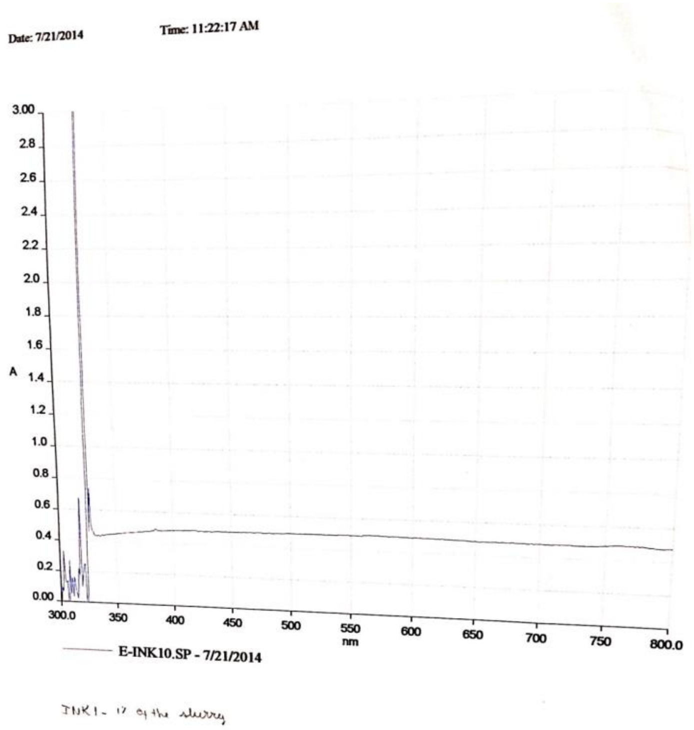
The third target, the development of a security ink a system, has been captured through the development of a proof of concept to monitor for traces of explosive compounds on ticket surfaces. The system also incorporates a track and trace mechanism and if the correct level of support is leveraged for the development of the concept, a viable solution to the very real issue of monitoring people and their possessions in a high throughput environment, such as a mass transit station, is of great possibility.

The ongoing developments at the Company in process improvement and optimisation are currently being complemented by activity on a second KTP (for which the candidate is Company Supervisor) to develop conductive inks for RFID tags, thereby consolidating the Company's position as a market leader in innovation within the printing industry.

Appendix 1 – Characterization Results

HL0301:

UV/VIS Spectrum



Date: 7/21/2014 Time: 11:22:17 AM

INK1 - 1% of the slurry

pH

Temperature: 24.6°C
pH: 4.22

Solid content

Mass empty: 47.2864 g
Mass wet: 48.3420 g

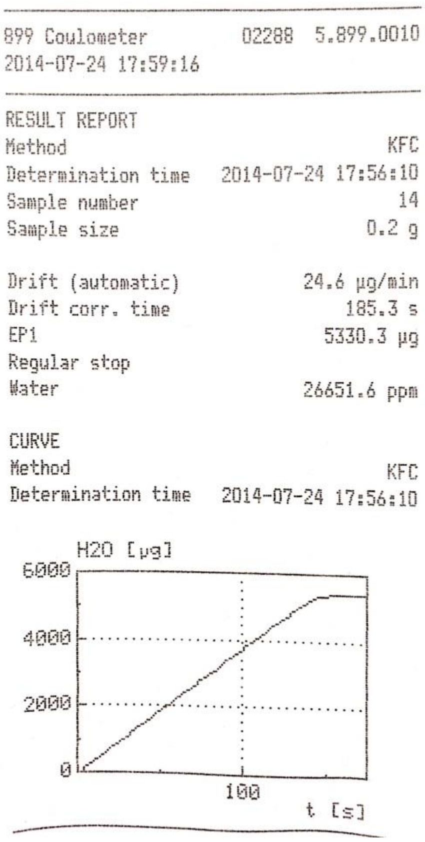
m_1	47.7404 g
m_2	47.7351 g
m_3	47.7350 g

% solid content ink 1 = 42,4972%

Water Content

Karl Fischer titration – 1% vol of the ink diluted with THF

Water content: 26651.6 ppm



```
899 Coulometer          02288  5.899.0010
2014-07-24 17:59:16

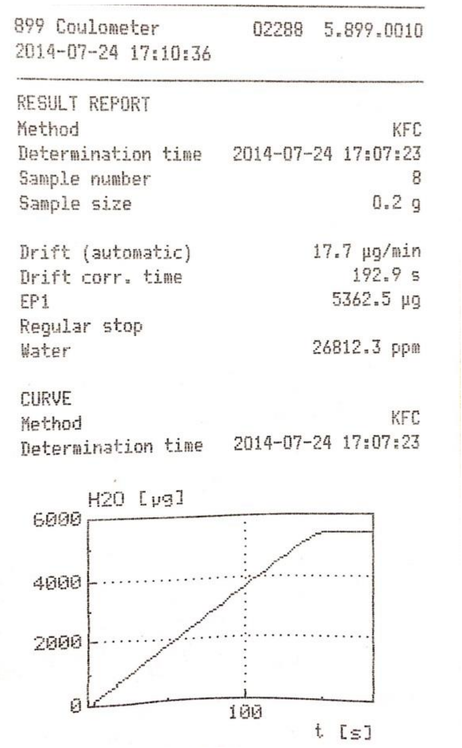
RESULT REPORT
Method                                KFC
Determination time    2014-07-24 17:56:10
Sample number                          14
Sample size                         0.2 g

Drift (automatic)             24.6 µg/min
Drift corr. time                  185.3 s
EP1                              5330.3 µg
Regular stop
Water                        26651.6 ppm

CURVE
Method                                KFC
Determination time    2014-07-24 17:56:10
```

Karl Fischer titration – 0.1% vol of the ink diluted with THF

Water content: 26812.3 ppm



```
899 Coulometer          02288   5.899.0010
2014-07-24 17:10:36

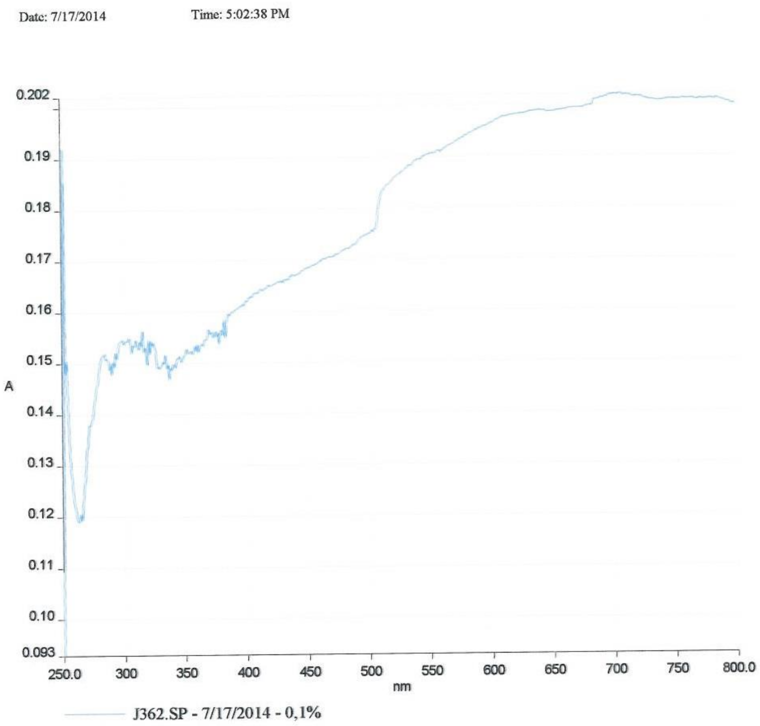
RESULT REPORT
Method                                 KFC
Determination time   2014-07-24 17:07:23
Sample number                            8
Sample size                          0.2 g

Drift (automatic)            17.7 µg/min
Drift corr. time                 192.9 s
EP1                             5362.5 µg
Regular stop
Water                         26812.3 ppm

CURVE
Method                                 KFC
Determination time   2014-07-24 17:07:23
```

FHL0201

UV/VIS Spectrum



pH Test:

Temperature: 24,1°C

pH: 6,62

Solid Content

Solid content was 31,689%

Water content - Karl Fischer:

The pure solution of THF had 620,5 ppm of water. For the FHL0201 ink the 1% solution had 2166,8 ppm of water, when this measure was repeated the content was 2236.7 ppm, and the concentration of 10% had 2261.6 ppm of water.

0% THF

```
899 Coulometer              02288  5.899.0010
2014-07-24 15:00:23

RESULT REPORT
Method                                    KFC
Determination time        2014-07-24 14:59:45
Sample number                              13
Sample size                             0.2 g

Drift (automatic)                 19.8 µg/min
Drift corr. time                       37.8 s
EP1                                   124.1 µg
Regular stop
Water                               620.5 ppm

CURVE
Method                                    KFC
Determination time        2014-07-24 14:59:45
```

1º INKS - 1%

```
899 Coulometer              02288  5.899.0010
2014-07-24 15:05:23

RESULT REPORT
Method                                    KFC
Determination time        2014-07-24 15:04:30
Sample number                              15
Sample size                             0.2 g

Drift (automatic)                 20.3 µg/min
Drift corr. time                       51.9 s
EP1                                   433.4 µg
Regular stop
Water                              2166.8 ppm

CURVE
Method                                    KFC
Determination time        2014-07-24 15:04:30
```

2º 1% - S Ink

```
899 Coulometer              02288  5.899.0010
2014-07-24 15:07:29

RESULT REPORT
Method                                    KFC
Determination time        2014-07-24 15:06:38
Sample number                              16
Sample size                             0.2 g

Drift (automatic)                 20.7 µg/min
Drift corr. time                       50.9 s
EP1                                   447.3 µg
Regular stop
Water                              2236.7 ppm

CURVE
Method                                    KFC
Determination time        2014-07-24 15:06:38
```

NKS - THF 10%

```
899 Coulometer              02288  5.899.0010
2014-07-24 15:03:09

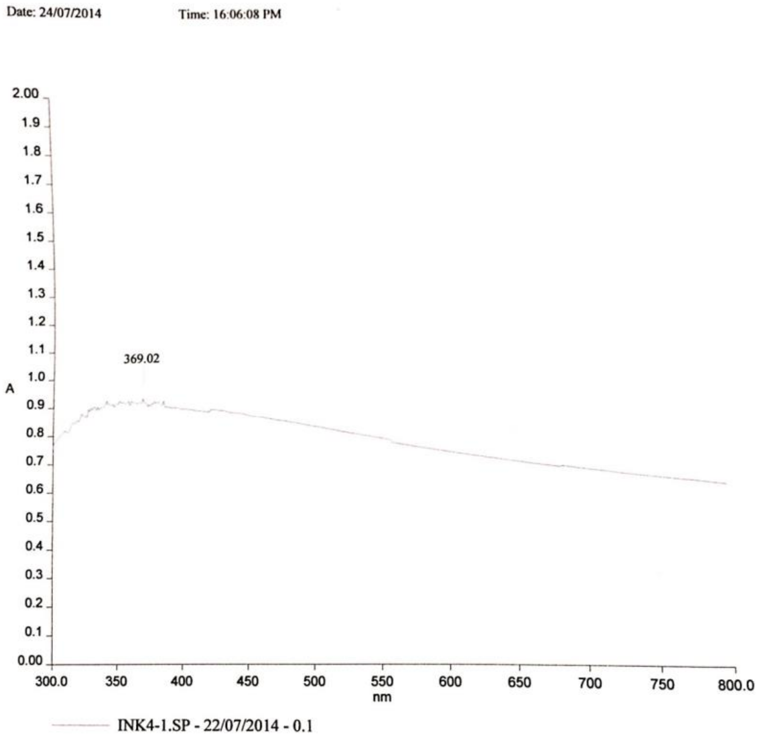
RESULT REPORT
Method                                    KFC
Determination time        2014-07-24 15:02:13
Sample number                              14
Sample size                             0.2 g

Drift (automatic)                 19.9 µg/min
Drift corr. time                       55.0 s
EP1                                   452.3 µg
Regular stop
Water                              2261.6 ppm

CURVE
Method                                    KFC
Determination time        2014-07-24 15:02:13
```

HH0104:

UV/Vis – 0.1% vol of ink

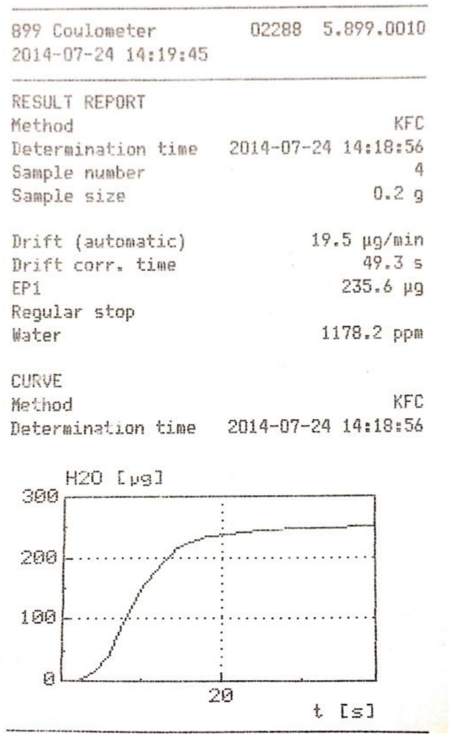


Date: 24/07/2014 Time: 16:06:08 PM

Water Content:

Karl Fischer titration – 1% vol of the ink diluted with THF

Water content: 1178.2 ppm



```
899 Coulometer          02288   5.899.0010
2014-07-24 14:19:45

RESULT REPORT
Method                                 KFC
Determination time     2014-07-24 14:18:56
Sample number                            4
Sample size                          0.2 g

Drift (automatic)             19.5 µg/min
Drift corr. time                    49.3 s
EP1                               235.6 µg
Regular stop
Water                           1178.2 ppm

CURVE
Method                                 KFC
Determination time     2014-07-24 14:18:56
```

pH

Temperature: 25.1°C
pH: 5.88

Solid content

Mass empty: 46.1107 g
Mass wet: 47.2261 g

m_1	46.6490 g
m_2	46.6398 g
m_3	46.6376 g
m_4	46.6375 g

% solid content ink 4 = 47,2297%

HH0401:

Solid Content:

% Solid content = 24.3761%

pH:

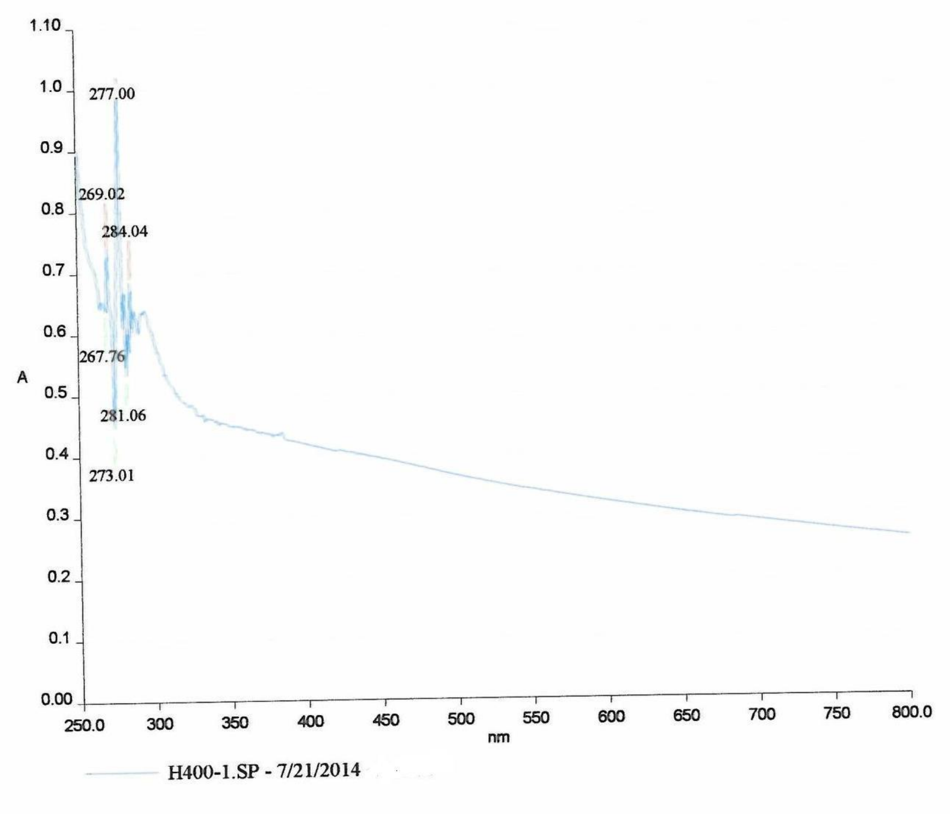
pH = 7.09, T = 25.9°C

Water Content:

THF – 773.6 ppm
1.0% – 402.2 ppm
0.1% – 483.1 ppm

HH0307:

UV-VIS:



Solid Content:

Empty flask for H400	42.8783 g		
Left on oven for 30 min at 90 °C	**Full flask**	**Ink weight**	
H400	44.9432 g	2.0649 g	
Left on oven for more 30 min at 90 °C	**Full flask**	**Ink weight**	
H400	43.7441 g	0.8658 g	
Left on oven for more 30 min at 90 °C	**Full flask**	**Ink weight**	
H400	43.7429 g	0.8646 g	
Left on oven for more 30 min at 90 °C	**Full flask**	**Ink weight**	**Solid percentage**
H400	43.7420 g	0.8637 g	41.83%

pH characterization

pH for H400 = 3.30

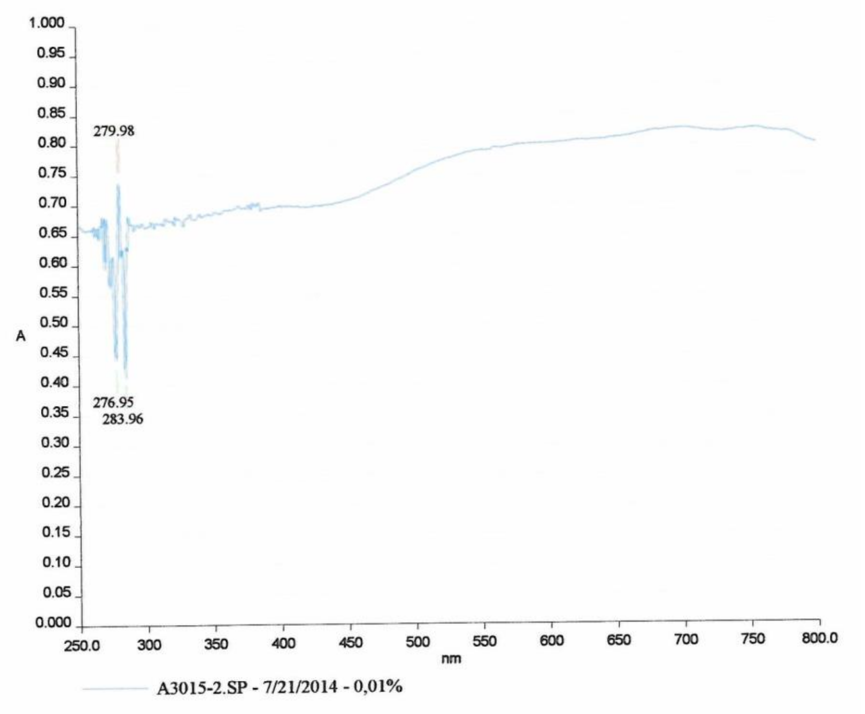
Water Content:

Ink 3 0.1% = 1928.0 ppm

Ink 3 1% = 13742.0 ppm

HL0104:

UV-VIS



Solid Content:

The solid content for the ink A3015 was 36.655%.

Empty flask for A3015	45.6165 g		
Left on oven for 30 min at 90 °C	**Full flask**	**Ink weight**	
A3015	47.1756 g	1.5591 g	
Left on oven for more 30 min at 90 °C	**Full flask**	**Ink weight**	
A3015	46.2158 g	0.5993 g	
Left on oven for more 30 min at 90 °C	**Full flask**	**Ink weight**	
A3015	46.2148 g	0.5983 g	
Left on oven for more 30 min at 90 °C	**Full flask**	**Ink weight**	**Solid percentage**
A3015	46.2146 g	0.5981 g	38.36%

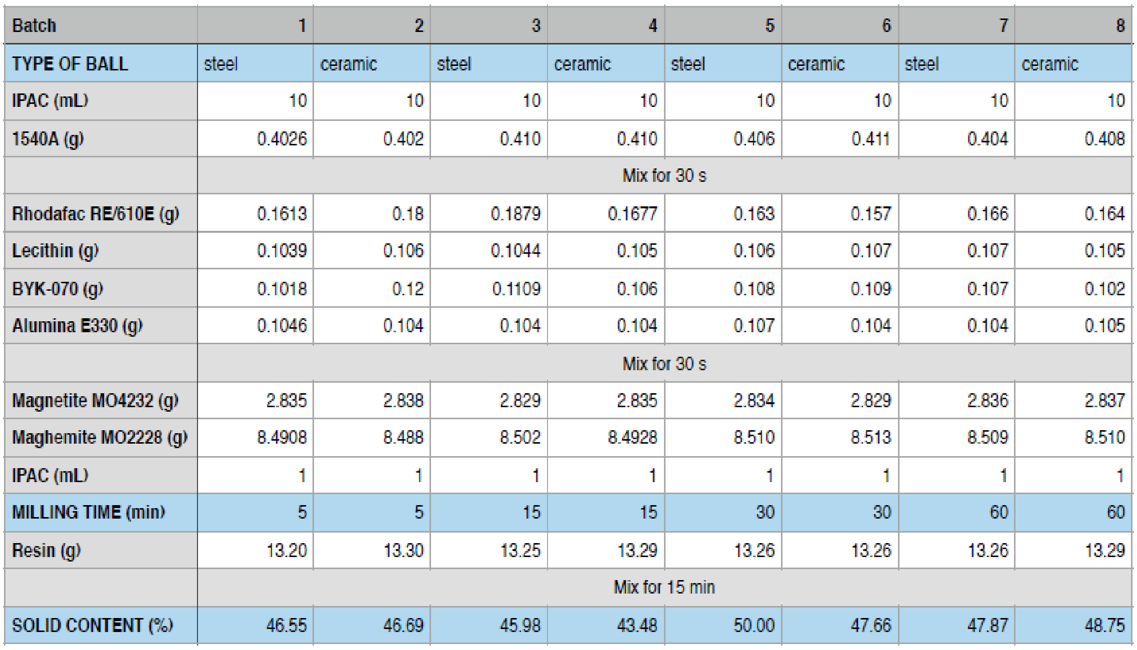
pH:

Temperature :25.1°C.
pH: 4.08

Water Content:

1% Solution: 1751.5 ppm of water, 10% solution had 970.4 ppm.

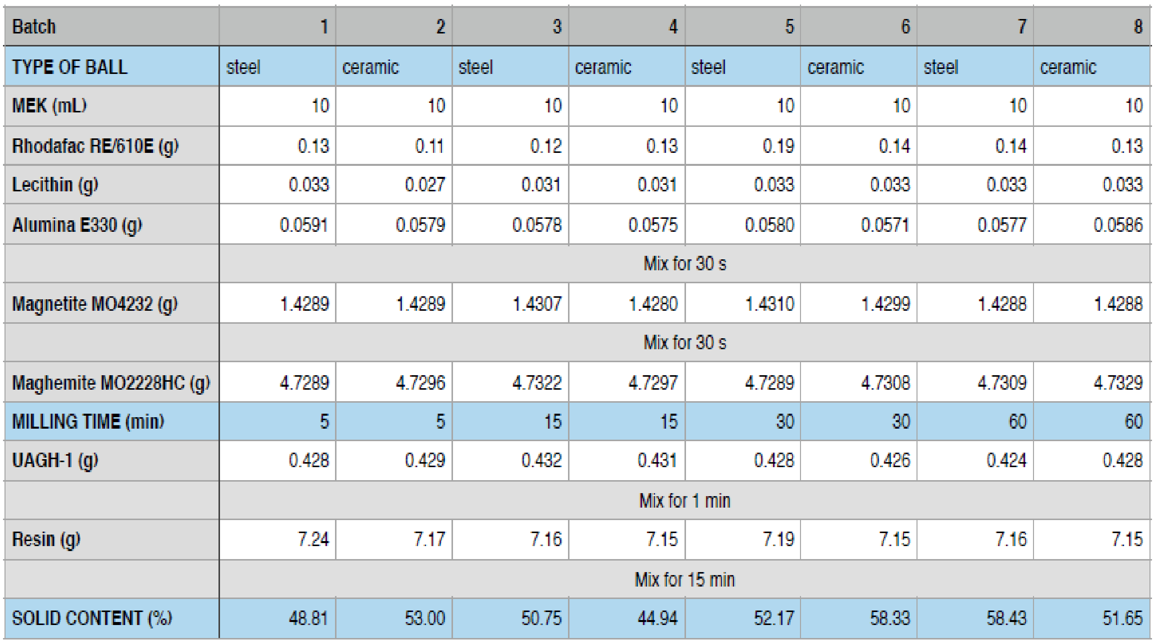
Appendix 2 – Formulations



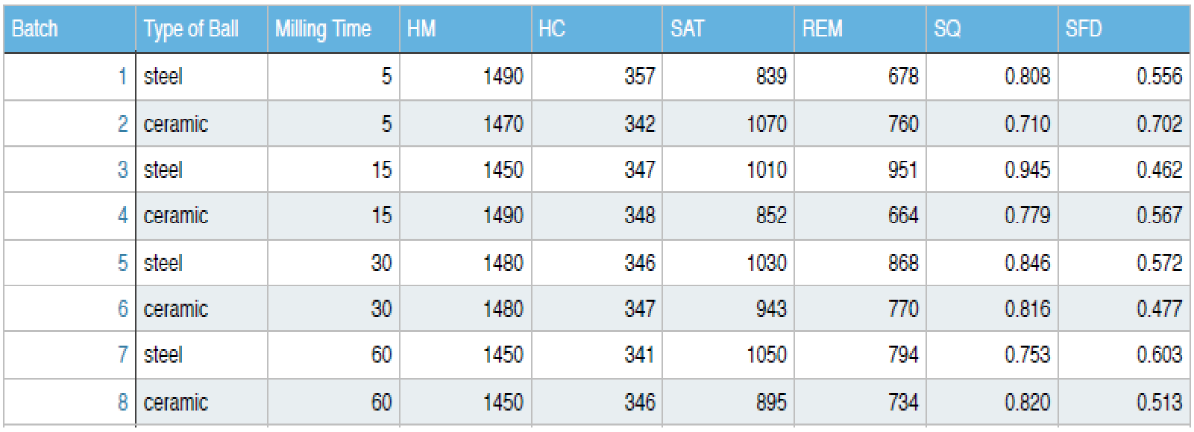
Batch	1	2	3	4	5	6	7	8
TYPE OF BALL	steel	ceramic	steel	ceramic	steel	ceramic	steel	ceramic
IPAC (mL)	10	10	10	10	10	10	10	10
1540A (g)	0.4026	0.402	0.410	0.410	0.406	0.411	0.404	0.408
	Mix for 30 s							
Rhodafac RE/610E (g)	0.1613	0.18	0.1879	0.1677	0.163	0.157	0.166	0.164
Lecithin (g)	0.1039	0.106	0.1044	0.105	0.106	0.107	0.107	0.105
BYK-070 (g)	0.1018	0.12	0.1109	0.106	0.108	0.109	0.107	0.102
Alumina E330 (g)	0.1046	0.104	0.104	0.104	0.107	0.104	0.104	0.105
	Mix for 30 s							
Magnetite MO4232 (g)	2.835	2.838	2.829	2.835	2.834	2.829	2.836	2.837
Maghemite MO2228 (g)	8.4908	8.488	8.502	8.4928	8.510	8.513	8.509	8.510
IPAC (mL)	1	1	1	1	1	1	1	1
MILLING TIME (min)	5	5	15	15	30	30	60	60
Resin (g)	13.20	13.30	13.25	13.29	13.26	13.26	13.26	13.29
	Mix for 15 min							
SOLID CONTENT (%)	46.55	46.69	45.98	43.48	50.00	47.66	47.87	48.75

HL0104 FORMULATION CERAMIC BALLS				
Batch	1	2	3	4
IPAC (mL)	10	10	10	10
1540A (g)	0.416	0.402	0.402	0.401
Mix for 30 s				
Rhodafac RE/ 610E (g)	0.2	0.16	0.2	0.18
Lecithin (g)	0.11	0.107	0.105	0.107
BYK-070 (g)	0.11	0.105	0.105	0.112
Alumina E330 (g)	0.106	0.107	0.104	0.105
Mix for 30 s				
Magnetite MO4232 (g)	2.832	2.832	20.833	2.83
Maghemite MO2228 (g)	8.493	8.492	8.494	8.491
IPAC (mL)	1	1	1	1
Milling time (min)	120	180	240	300
Resin (g)	13.25	13.26	13.15	13.26
Mix for 15 minutes				
Solid Content (%)	44	42	47.6	47.5

Table 1: Weightings and Solid Contents HL0104 for 120, 180, 240 and 300 minutes



Batch	1	2	3	4	5	6	7	8
TYPE OF BALL	steel	ceramic	steel	ceramic	steel	ceramic	steel	ceramic
MEK (mL)	10	10	10	10	10	10	10	10
Rhodafac RE/610E (g)	0.13	0.11	0.12	0.13	0.19	0.14	0.14	0.13
Lecithin (g)	0.033	0.027	0.031	0.031	0.033	0.033	0.033	0.033
Alumina E330 (g)	0.0591	0.0579	0.0578	0.0575	0.0580	0.0571	0.0577	0.0586
	Mix for 30 s							
Magnetite MO4232 (g)	1.4289	1.4289	1.4307	1.4280	1.4310	1.4299	1.4288	1.4288
	Mix for 30 s							
Maghemite MO2228HC (g)	4.7289	4.7296	4.7322	4.7297	4.7289	4.7308	4.7309	4.7329
MILLING TIME (min)	5	5	15	15	30	30	60	60
UAGH-1 (g)	0.428	0.429	0.432	0.431	0.428	0.426	0.424	0.428
	Mix for 1 min							
Resin (g)	7.24	7.17	7.16	7.15	7.19	7.15	7.16	7.15
	Mix for 15 min							
SOLID CONTENT (%)	48.81	53.00	50.75	44.94	52.17	58.33	58.43	51.65



Batch	Type of Ball	Milling Time	HM	HC	SAT	REM	SQ	SFD
1	steel	5	1490	357	839	678	0.808	0.556
2	ceramic	5	1470	342	1070	760	0.710	0.702
3	steel	15	1450	347	1010	951	0.945	0.462
4	ceramic	15	1490	348	852	664	0.779	0.567
5	steel	30	1480	346	1030	868	0.846	0.572
6	ceramic	30	1480	347	943	770	0.816	0.477
7	steel	60	1450	341	1050	794	0.753	0.603
8	ceramic	60	1450	346	895	734	0.820	0.513

Table 2: BH Looper HL0301

Appendix 3 – BBP MAPP

Major Accident Prevention Policy

This document has been designed so as to implement the Control of Major---Accident Hazards involving Dangerous Substances (Seveso III Directive 2012/18/EU).

1. Statement of Intent

Bemrose Booth Paragon Ltd. acknowledges that its manufacturing activity is holds potential major accident or process safety risks to people (employees, contractors, visitors and neighbours), the environment and its business. It is the policy of Bemrose Booth Paragon Ltd. to manage its major hazards so as to provide a high level of protection to all resources – human and the environment, that are liable to be otherwise adversely affected by major accidents. Bemrose Booth Paragon Ltd. is committed to managing its activities (such as process design, control and construction, operation and facility maintenance, and inspection) responsibly, to ensure all reasonable measures are taken to prevent major incident. It is a high priority in Bemrose Booth Paragon Ltd.'s objectives to limit the consequence to people and the environment of any major accident that may occur, despite the preventative measures taken. This is achieved through the application of the Bemrose Booth Paragon Ltd, Health, Safety and Environment Management System, to meet with the general Bemrose Booth Paragon Ltd Health, Safety and Environment Policy in compliance with Bemrose Booth Paragon Ltd. Implementation of this is through an established reviewing and auditing of the procedures as documented within the management system, and which identifies the specific measures taken for major hazard control.

2. Safety Management System

Bemrose Booth Paragon Ltd. are committed in the provision of all necessary financial, material and human resources to achieve the aims and principles of action with respect to the prevention of major accidents. Bemrose Booth Paragon Ltd. will adopt an approach of mindful process safety leadership through defining the roles and responsibilities of personnel at all levels involved in the management of the major hazards; provide, assess and validate the regular training of personnel to ensure they are competent in working with a major hazard; implement systematic risk identification and evaluation protocols; keep documented records of procedures and instructions for the safe operation of activities; enable process safety and minimization of environment damage as a founding principle in which new plant, equipment and process design considerations are based to manage risks; maintain emergency plans and emergency procedures; measure compliance with the Statement of Intent through Health, Safety and Environment assurance procedures through reviews with appropriate updating of documentation; audit Health, Safety and Environment performance regularly so that this information is available to the public through The Freedom of Information Act 2000 (c.36).

2.1 Roles and Responsibilities

The Health, Safety and Environment Management Committee (HSEMC) is set up to function as planning and controlling members for the Safety, Health and Environment Management System of Bemrose Booth Paragon Ltd. The team members of the HSEMC assist the Bemrose Booth Paragon Ltd. Board in prioritizing Health, Safety and Environment strategies, resourcing Health, Safety and Environment initiatives, thus providing the Board with an independent and objective review of how effective is the Health, Safety and Environment Management Strategy (HSEMS), including how well it is implemented. The HSEMC is committed to continually developing and monitoring the effectiveness of the HSEMS to ensure that statutory and regulatory requirements continue to be met. The Health, Safety and Environment Management Committee is set up to take into account:

- Clarity of roles and responsibilities of each member,
- Experiences of Committee members regarding challenges, issues, concerns or opportunities,
- Reviewing the HSEMS periodically to ensure continued suitability, adequacy and effectiveness,
- Actions for further improvement of the HSEMS are assessed and evaluated,
- Resourcing and prioritizing of all Health, Safety and Environment initiatives within the HSEMS of Bemrose Booth Paragon Ltd.
- The co-ordination and management of all Bemrose Booth Paragon Ltd. Health, Safety and Environment initiatives,
- The on-going reporting of status of the HSEMS of Bemrose Booth Paragon Ltd.

For the major accident risks identified (potential fire and/or explosion within the HMI Process Building, or of the solvent inventory stored externally to the HMI Process Building) the following employees are involved from the management level during emergency. Responsibility for hazard identification is made by all workforce employees; accountability of major incidents is held by the General Manager/CEO.

Table 1: Roles and Responsibilities in the event of an incident.

Role	Responsibility
Production Manager Graham Winship	Ensure production is stopped immediately
Quality and Environmental Managers Lisa Leonard/Graham Winship	Liaise with emergency personnel
Planning Manager Martin Waudby	Liaise with Bemrose Booth Paragon Ltd. Executive Board
Fire and Emergency Wardens Various	Liaise with workforce and emergency personnel, ensure relevant evacuation
Health and Safety Officer Lee Guest	Review the Safety Systems in place
Technical Manager Jamie Parker	Liaise with Production Manager and other relevant management figures.

2.2 Selection and Training

The selection and placement of employees will take into consideration their competency and expertise in health, safety and environment protection. Training in fire safety management will be provided to all employees so that they have a high level of both skill and regard for the safety and health of themselves and others, and for the protection of the environment. The Health and Safety Officer will be required to hold a NEBOSH Certificate in Health and Safety. The Environment Manager will be required to hold a NEBOSH Certificate in Environment Management. Training and its validation will be reviewed regularly.

2.3 Hazard Identification and Risk Assessment

Bemrose Booth Paragon Ltd. will adopt a systematic approach in the identification and evaluation of risk, in compliance with BS EN ISO 31000:2009, using a risk reduction hierarchy, with inherent safety as a paramount and guiding principle. It will develop, implement and maintain protocols for the limitation of consequences of major hazards associated with Bemrose Booth Paragon Ltd.'s business activities, equipment and schemes designed in both normal and exceptional circumstances, as far as is reasonably practical. All control measures will be recorded so that the risks are clearly understood by Bemrose Booth Paragon Ltd.

2.4 Safe Operation & Design and Modifications of Installations

A culture of commitment to the achievement of a high standard of safety and environmental performance involving staff at all levels will be fostered and encouraged at Bemrose Booth Paragon Ltd. COSHH databases, risk and issue registers will be available for all staff to access. Standard operating procedures will be reviewed in the light of risk and issue registers on a monthly basis by the Health and Safety Officer. All locations (HMI Process Building, internal and external storage, and remainder of factory/warehouse) will report health, safety and environment performance on a monthly basis, to be reviewed by the Bemrose Booth Paragon Ltd. Executive Board. Incidents and public complaints shall be recorded and investigated promptly, and the appropriate corrective action will be taken to prevent re-occurrence. Updates to operating procedures will be communicated to the workforce through line management control, and feedback on corrective action will be employed to feed-forward into iteratively developing those operating procedures, if appropriate. Design of new equipment and processes will be managed through guidance *via* statutory and regulatory requirements. All new equipment/process instrumentation will have risk assessments undertaken.

2.5 Emergency Plans

The nature, scale and consequence of all reasonably foreseeable emergencies shall be identified and documented. Emergency procedures pertaining to these will be developed and displayed, with appropriate arrangements made in association/with the public emergency services. Communication of emergency procedures and plans will be annually, with annual rehearsal and review.

2.6 Compliance

The continual monitoring of health, safety and environmental performance to assess compliance with the MAPP objectives and the implementation of corrective action will be achieved through the active monitoring of the safety, health and environmental management process, and the reactive monitoring of the reporting procedures of issues, risks, near misses, and system failures. These will be subjected to annual review by the Bemrose Booth Paragon Ltd. Executive Board, and through the periodic external audit of the performance statistics and standards.

2.7 Review

A formal review of the MAPP and the efficacy of the Health, Safety and Environment Management System will be undertaken quinquennially by the Managing Director/General Manager/CEO. Deficiencies identified during this review will be formally recorded, their implications assessed and corrective actions prioritized, implemented and recorded. A re-issue of the MAPP and the HSEMS will take place after every review.

Signed ____

Name ____

Position __________GM/MD/CEO_____________________

Date ____

Appendix 4 – What-If Analysis

Situation/What If	Hazard	Safeguard	Recommendation
Piping leaks	High velocity release of slurry that could form pool fire	Regular monthly maintenance checks to determine condition of pipes and check for any leaks.	Ensure all pipework is clean and free of slurry externally so that full examinations can be carried out.
Piping becomes fouled	Increase in velocity of slurry to maintain constant volumetric flow rate	No current safeguard in place.	Regular pipe stripping and checks to remove any accumulation/fouling in the vessel.
Piping is corroded (internally or externally)	Formation of weak point that could lead to high velocity release of slurry that could form pool fire	Currently, external corrosion is monitored for vessel and also cooling pipe systems.	Monthly inspection of pipework internals.
Piping supports fail	Slurry or cooling pipes will fall out of position causing leaks and therefore fire/toxic release hazard	No safeguard in place.	Pipework is currently under temporary support for chiller. Ensure all pipework is reinforced at critical points.
Piping is subject to external impact	High velocity release of slurry that could form pool fire	Prevention of vehicles/forklifts in process room. Current piping supports.	Reduce amount of stored material in HMI room to increase space for movement with pallets. Find an appropriate storage area external to HMI.
Flow increases	Recirculation speed	Operating procedure	Re-train and re-enforce importance of the

	increases – slurry splashes up the back of the machine into mechanical components – potential for breakdown or fire,	indicates regulator pressure settings for recirculation process. These are not to be exceeded.	operating procedure. Set limiters on regulators so that max process pressure required for dispensing/recirculation cannot be exceeded.
Flow is reversed or redirected	Flow cannot be reversed but can be re-directed for dispensing. Potential release of slurry forming flammable vapour cloud	No current physical safeguard	Install padlocks on dispensing valves.
Piping is subject to flow or pressure surges	Flow is through diaphragm pump operating through consistent surges of pressure. Large surges through regulator failure may result in pipe failure and leaks	Regulator ensures constant air pressure. No safeguard against regulator failure.	Inspect regulators monthly
Piping is subject to vibration	May cause cracks/leaks in excessive vibration	Piping supports resist vibration	Ensure maintenance encompasses piping support condition.
Valves are left open	Vessels could leak entire contents forming	No safeguard currently on vessel valves but	Padlock vessel valves.

	flammable vapour cloud.	padlocks on solvent valves.	
Valves become fouled	Valves may not be able to be opened fully or at all leading to a pressure build up. May not be able to close a valve that has been opened.	Back up valves over course of pipeline help to relieve pressure. This does not apply to the last two valves so there is no safeguard system.	Regular maintenance will stop attritor media getting into pipelines. Regular maintenance and cleaning of pipelines prevents accumulation.
Pump fails to start or stop on demand	Potential for high velocity release of slurry	No safeguard in place	Install emergency stop on airline.
Pump is subject to freezing conditions	Damage to diaphragm inside pump.	Pump is located inside the process building.	New extraction and LEV system will maintain

Appendix 5: Example Operating Procedure – 30s Attritor as shown on HMI Wiki.

Operating Procedure Number	Machine	Prepared By	Custodian	References	Issue Number	Issue Date
HMI OP001	Attritor 1 (30s)	Haydn Ward	Quality Manager	***	1.1	29.05.17

Scope

This standard operating procedure provides the operating instructions for Attritor 1 (30s). The following procedure applies to loading, general operation, manufacturing features and unloading of the machine. Incorporated in this OP is information regarding the correct switch on/shut down procedure, general operation, maintenance and health and safety information.

Summary of the Process

The attrition process involves the wet milling of magnetic pigment in solvent, in the presence of the surfactants, defoamer and head cleaner, to reduce overall iron oxide particle size to the desired, uniform level, taking approximately 5 hours. The mixing process involves the production of a resin, where the binders and solvent are homogenised in the mixer for approximately 2 hours. Once the resin mixture is ready, it is transferred into the attritor for the final milling phase. The final stage takes approximately one hour, yielding uniform ink slurry to be dispensed and dispatched for coating. The bespoke HMI software directs the operator through each of the stages in a clear and efficient manner.

Safety

Appropriate PPE must be worn relating to the chemicals stated in the bill of materials (BOM) for the particular slurry type. Each MSDS must be studied to determine the level of PPE required for each stage of the process. Before entering the HMI room the minimum required PPE must be worn subject to the checklist provided. The Sole Mate II static discharge system must be used upon entry, signing the log book. Overalls, goggles and anti-static safety shoes must be worn at all times inside the HMI room. Gloves, face visor and dust mask/respirator should be worn when dealing with slurry/solvents during manufacture or cleaning out the vessel. Hands or loose clothing must always be kept away from moving parts. Always ensure the work area is kept clean and tidy with no obstructions.

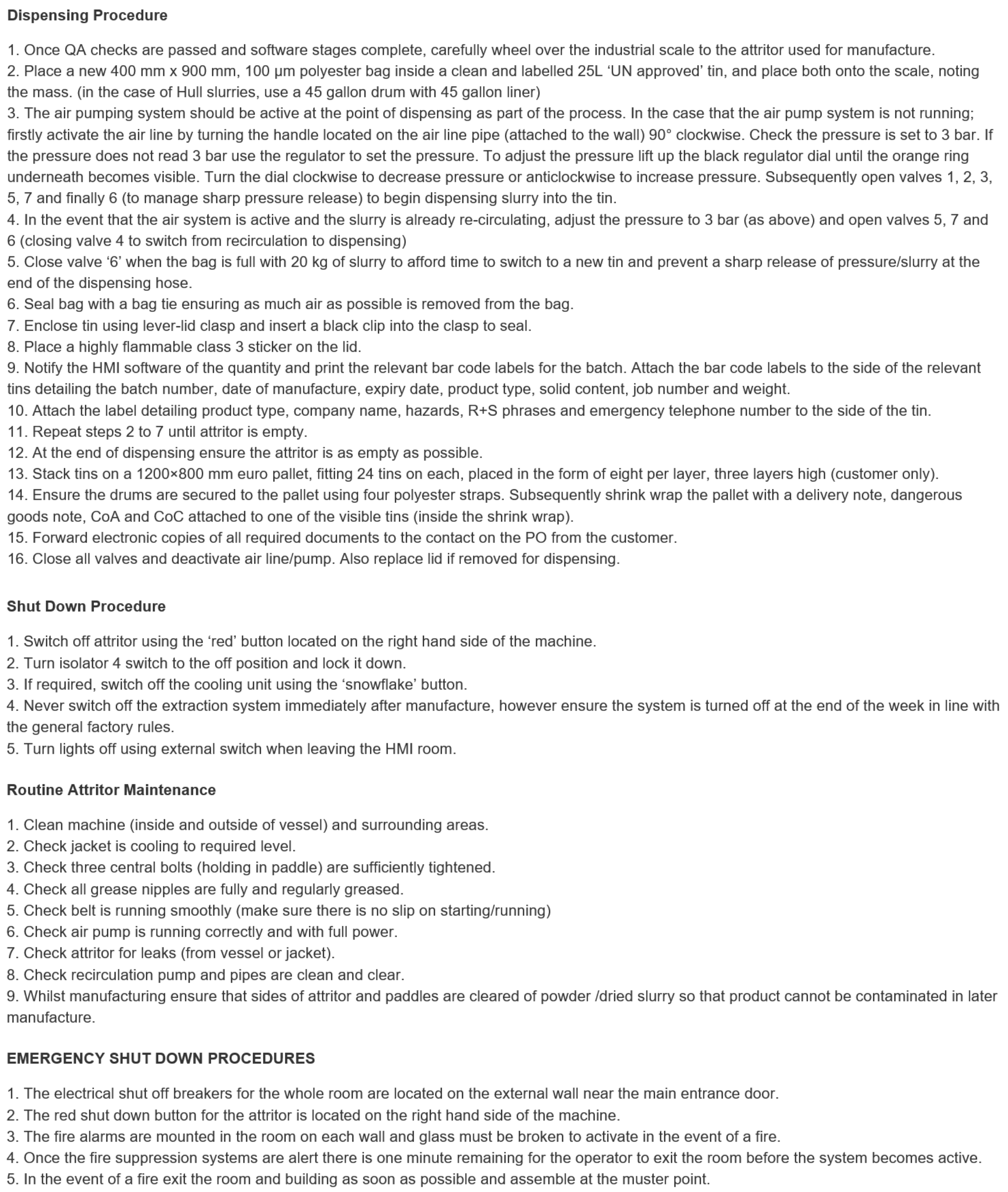
AT ANY TIME WHEN A SLURRY SAMPLE IS REQUIRED FROM AN ATTRITOR, THE ATTRITOR MUST BE SWITCHED OFF FIRST.

Set Up Procedure

1. Before handling, weighing and dispensing any materials or operating any machines all relevant Personal Protective Equipment (PPE) MUST be in place. (Refer to relevant MSDS)
2. First exit the HMI room and activate the externally located cooling unit by pressing the ‘snowflake’ button. Ensure the system is set to 8 °C so that the product will remain at optimum manufacturing temperature during the process (adjust as required during process based on temperature monitoring results - HMI TPR010).
3. Return to the HMI room and switch isolator 1 from the ‘off’ to the ‘on’ position, unlocking first if required.
4. Ensure valves 1 to 7 are closed before starting manufacture.
5. Change the dispensing filter if required – check sheet on wall (changed every three batches or product change). Follow filter changing procedure HMI WI 004.
6. Follow the on screen instuctions of the HMI software to set up the job and perform any pre-manufacture tests.
7. When prompted by the software, fill the attritor with the appropriate solvent using the solvent management system panels – never mill with a dry vessel. Always check prior to the transfer, using the solvent monitoring documents that the desired quantity of solvent is present in the current barrel to meet the demand for the volume requested by the solvent management panel.
8. Ensure the attritor is set to the lowest possible speed and press the ‘start/green’ button on the right hand side of the machine to activate the motor/pulley mechanism and subsequently engage the clutch to connect the paddle and begin milling. The attritor can be turned up to operational speed (50 rpm unless otherwise stated) once running.
9. Place initials in the ‘weighed’ and ‘added’ boxes in the BMR during manufacture to identify the personnel responsible for each task.

Recirculation Procedure

1. Upon passing the dispersion QA test the slurry must be re-circulated through the external pipes attached to the attritor. This is powered by an air driven ATEX rated positive displacement diphragm pumping system.
2. Firstly activate the air line by turning the handle located on the air line pipe (attached to the wall) 90° clockwise.
3. Check the pressure is set to 2 bar. If the pressure does not read 2 bar use the regulator to set the pressure. To adjust the pressure lift up the black regulator dial until the orange ring underneath becomes visible. Turn the dial clockwise to decrease pressure or anticlockwise to increase pressure.
4. Once the air pump is active, to re-circulate turn valves 1, 2, 3, and 4 90° so that they are parallel to the external pipes.
5. The recirculation process will now continue until dispensing.



Dispensing Procedure

1. Once QA checks are passed and software stages complete, carefully wheel over the industrial scale to the attritor used for manufacture.
2. Place a new 400 mm x 900 mm, 100 µm polyester bag inside a clean and labelled 25L 'UN approved' tin, and place both onto the scale, noting the mass. (in the case of Hull slurries, use a 45 gallon drum with 45 gallon liner)
3. The air pumping system should be active at the point of dispensing as part of the process. In the case that the air pump system is not running; firstly activate the air line by turning the handle located on the air line pipe (attached to the wall) 90° clockwise. Check the pressure is set to 3 bar. If the pressure does not read 3 bar use the regulator to set the pressure. To adjust the pressure lift up the black regulator dial until the orange ring underneath becomes visible. Turn the dial clockwise to decrease pressure or anticlockwise to increase pressure. Subsequently open valves 1, 2, 3, 5, 7 and finally 6 (to manage sharp pressure release) to begin dispensing slurry into the tin.
4. In the event that the air system is active and the slurry is already re-circulating, adjust the pressure to 3 bar (as above) and open valves 5, 7 and 6 (closing valve 4 to switch from recirculation to dispensing)
5. Close valve '6' when the bag is full with 20 kg of slurry to afford time to switch to a new tin and prevent a sharp release of pressure/slurry at the end of the dispensing hose.
6. Seal bag with a bag tie ensuring as much air as possible is removed from the bag.
7. Enclose tin using lever-lid clasp and insert a black clip into the clasp to seal.
8. Place a highly flammable class 3 sticker on the lid.
9. Notify the HMI software of the quantity and print the relevant bar code labels for the batch. Attach the bar code labels to the side of the relevant tins detailing the batch number, date of manufacture, expiry date, product type, solid content, job number and weight.
10. Attach the label detailing product type, company name, hazards, R+S phrases and emergency telephone number to the side of the tin.
11. Repeat steps 2 to 7 until attritor is empty.
12. At the end of dispensing ensure the attritor is as empty as possible.
13. Stack tins on a 1200×800 mm euro pallet, fitting 24 tins on each, placed in the form of eight per layer, three layers high (customer only).
14. Ensure the drums are secured to the pallet using four polyester straps. Subsequently shrink wrap the pallet with a delivery note, dangerous goods note, CoA and CoC attached to one of the visible tins (inside the shrink wrap).
15. Forward electronic copies of all required documents to the contact on the PO from the customer.
16. Close all valves and deactivate air line/pump. Also replace lid if removed for dispensing.

Shut Down Procedure

1. Switch off attritor using the 'red' button located on the right hand side of the machine.
2. Turn isolator 4 switch to the off position and lock it down.
3. If required, switch off the cooling unit using the 'snowflake' button.
4. Never switch off the extraction system immediately after manufacture, however ensure the system is turned off at the end of the week in line with the general factory rules.
5. Turn lights off using external switch when leaving the HMI room.

Routine Attritor Maintenance

1. Clean machine (inside and outside of vessel) and surrounding areas.
2. Check jacket is cooling to required level.
3. Check three central bolts (holding in paddle) are sufficiently tightened.
4. Check all grease nipples are fully and regularly greased.
5. Check belt is running smoothly (make sure there is no slip on starting/running)
6. Check air pump is running correctly and with full power.
7. Check attritor for leaks (from vessel or jacket).
8. Check recirculation pump and pipes are clean and clear.
9. Whilst manufacturing ensure that sides of attritor and paddles are cleared of powder /dried slurry so that product cannot be contaminated in later manufacture.

EMERGENCY SHUT DOWN PROCEDURES

1. The electrical shut off breakers for the whole room are located on the external wall near the main entrance door.
2. The red shut down button for the attritor is located on the right hand side of the machine.
3. The fire alarms are mounted in the room on each wall and glass must be broken to activate in the event of a fire.
4. Once the fire suppression systems are alert there is one minute remaining for the operator to exit the room before the system becomes active.
5. In the event of a fire exit the room and building as soon as possible and assemble at the muster point.

Appendix 6 – MSDS Example

SECTION 1: PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME: HL0301 Magnetic Ink Slurry
SYNONYMS: Low Coercivity Magnetic Ink Slurry
PRODUCT CODES: HL0301

MANUFACTURER: BemroseBooth Paragon Ltd
DIVISION: Hull
ADDRESS: Bemrose Booth Paragon Hull
Stockholm Road
Sutton Fields
Hull
HU7 0XY

EMERGENCY PHONE: + 44 (0) 1482 826343

CHEMICAL FAMILY: Organic solvent; Tetrahydrofuran, Methyl Ethyl Ketone

PRODUCT USE: Coating/printing onto various substrates utilized for ticketing applications in locomotive, automotive and aeronautical travel.

SECTION 2: HAZARDS IDENTIFICATION

Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008

Flammable liquids (Category 3), H225
Eye irritation (Category 2), H319
Specific target organ toxicity - single exposure (Category 3), H336
For the full text of the H-Statements mentioned in this Section, see Section 16.

Classification according to EU Directives 67/548/EEC or 1999/45/EC

F	Highly flammable	R11 R66 R67
Xi	Irritant	R36

For the full text of the R-phrases mentioned in this Section, see Section 16.

Label elements
Labelling according Regulation (EC) No 1272/2008

Pictogram:

Signal word Danger

Hazard statement(s)

H225	Highly flammable liquid and vapour.
H319	Causes serious eye irritation.
H336	May cause drowsiness or dizziness.

Precautionary statement(s)

P210	Keep away from heat/sparks/open flames/hot surfaces. - No smoking.

P261	Avoid breathing dust/ fume/ gas/ mist/ vapours/ spray.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard information (EU)

EUH066	Repeated exposure may cause skin dryness or cracking.

SECTION 3 COMPOSITION/INFORMATION ON INGREDIENTS

Potentially dangerous substances under the EU Directive 67/548/EEC**.**

Ingredient	Index No.	Cas No.	Concentration (%)	Hazard Symbols	R Phrases
Tetrahydrofuran	603-025-00-0	109-99-9	10-25	F, Xi	11, 36, 66, 67
Methyl Ethyl Ketone	606-002-00-3	78-93-3	50-75	F, Xi	11, 36, 66, 67

Refer to Section 16 for full R phrase explanations.

SECTION 4: FIRST AID MEASURES

General advice: Consult a physician. Show this safety data sheet to the doctor in attendance.
If inhaled: If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.
In case of skin contact: Wash off with soap and plenty of water. Consult a physician. DO NOT use solvent or thinners.
In case of eye contact: Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.
If swallowed: Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician/Call a doctor Immediately.

Most important symptoms and effects, both acute and delayed:
The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

Indication of any immediate medical attention and special treatment needed
No data available

SECTION 5: FIRE-FIGHTING MEASURES

EXTINGUISHING MEDIA: Alcohol-resistant foam, dry chemical or carbon dioxide.

UNSUITABLE EXTINGUISHING MEDIA: Water spray

SPECIAL FIRE FIGHTING PROCEDURES: Wear self-contained breathing apparatus for fire fighting

UNUSUAL FIRE AND EXPLOSION HAZARDS: Carbon oxides, traces of hydrochloric acid

HAZARDOUS DECOMPOSITION PRODUCTS: Use water spray to cool unopened containers

RECOMMENDATIONS: A fire will produce a thick, black smoke. Exposure to decomposition products may comprise health risks. Wear appropriate breathing apparatus for fire-fighting. Prevent the effluent from entering any drains.

SECTION 6: ACCIDENTAL RELEASE MEASURES

ACCIDENTAL RELEASE MEASURES:

Personal precautions, protective equipment and emergency procedures:
Use personal protective equipment. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Remove all sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations. Vapours can accumulate in low areas.
For personal protection see section 8.

Environmental precautions

Contain and collect spillages with non-combustible absorbent materials such as sand, earth or vermiculite to contain the spillage, and then collect with an electrically protected vacuum cleaner or by wet-brushing and place in container for disposal according to local regulations (see section 13). Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

Methods and materials for containment and cleaning up
Clear preferably with a detergent. Avoid the use of solvents.

Reference to other sections
See section 13. for disposal.

SECTION 7: HANDLING AND STORAGE

HANDLING AND STORAGE:

Precautions for safe handling
Avoid inhalation of vapour or mist. Ensure vapour is aspirated at the source of their emission as well as having a general ventilation of air in the vicinity of their use. Wear suitable respiratory protection to avoid exposure to vapour concentrations higher than the quoted exposure guidelines detailed in section 8.

The vapour is heavier than air. The vapour may stay stationary for a long time and form an explosive mixture with air. Prevent the development of flammable or explosive concentrations in air.

Use the product away from naked flames and keep away from all sources of ignition. Ensure electrical equipment is protected.

The product may become electrostatically charged. Take measures to prevent the build-up of electrostatic charge. It is recommended that using personnel wear appropriate footwear and antistatic clothes, and to discharge themselves on an earthed conductor prior to using the product.

Keep the product firmly closed and away from sources of heat, sparks and naked flames.

Avoid contact with skin and eyes. Ensure personnel wear protective clothing, gloves and safety googles. See section 8.

It is forbidden to smoke, eat or drink in the vicinity of the product or its use.

Never open the product using pressure, and always keep the product in its original containers.

Ensure that workforce regulations are observed.

OTHER PRECAUTIONS:
See section 2.

Conditions for safe storage, including any incompatibilities
Store in a cool place (10 to 35 °C). Keep container tightly closed in a dry and well-ventilated place and away from all sources of ignition, heat and direct sunlight.

Keep product away from strong oxidants and any material that is strongly acidic or alkaline.

Do not smoke near the product. Strictly no access to unauthorised personnel. Containers which are opened must be carefully resealed and kept upright to prevent leakage.

Specific end use(s)
Apart from the uses mentioned in section 1, no other specific uses are stipulated

SECTION 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

ENGINEERING CONTROLS:
Ensure the product is kept in a solvent resistant and tightly sealed tin, under atmospheric pressure. Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of the working day.

VENTILATION :
Air exchange/extraction must be implemented in a room where a high concentration of product vapour is present

RESPIRATORY PROTECTION:
Where risk assessment shows air-purifying respirators are appropriate, use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU). Masks incorporating an organic solvent filter must be worn when handling this product if vapour release is above the upper level.

EYE PROTECTION:
Face shield and safety glasses Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU). Laboratory goggles with peripheral protection must be worn at minimum, preferably goggles that seal around the eyes.

SKIN PROTECTION:
Handle with gloves (latex/nitrile). Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands. The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and
the standard EN 374 derived from it. If used in solution, or mixed with other substances, and under conditions which differ from EN 374,
contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any
specific use scenario.

OTHER PROTECTIVE CLOTHING OR EQUIPMENT:
Wear impervious clothing. Flame retardant, antistatic overalls or laboratory coats must be worn and after use cleaned on a regular basis. The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace. Antistatic footwear is recommended to ensure protection against ignition.

WORK HYGIENIC PRACTICES:
Always wash hands thoroughly after contact or use.

Control of environmental exposure

Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

EXPOSURE GUIDELINES:

Tetrahydrofuran:

STEL(1)		**LTEL(2)**	
ppm	mg/m^3	ppm	mg/m^3
100	300	50	150

Methyl Ethyl Ketone:

STEL(1)		**LTEL(2)**	
ppm	mg/m^3	ppm	mg/m^3
300	900	200	600

(1) STEL: short term exposure limit (15 min); Europe. Commission Directive 2000/39/EC establishing a first list of indicative occupational exposure limit values.

(2) LTEL: long term exposure limit (8h/day); Europe. Commission Directive 2000/39/EC establishing a first list of indicative occupational exposure limit values.

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE:		**Brown-black**
ODOR:		**Light ethereal**
PHYSICAL STATE:		**Viscous liquid**
pH AS SUPPLIED:	**Not applicable**	
pH (Other):	**Not applicable**	
BOILING POINT:		**Not available**
MELTING POINT:		**Not available**
VAPOR PRESSURE (mmHg):	**Not available**	
VAPOR DENSITY (AIR = 1):		**Not available**
SPECIFIC GRAVITY (H2O = 1):	**Not available**	
EVAPORATION RATE:	**Not available**	
SOLUBILITY IN WATER:		**Partially miscible**
PERCENT SOLIDS BY WEIGHT:	**40-50**	
PERCENT VOLATILE:		
BY WT @	**50-60**	
F:		**68**
C:		**20**
MOLECULAR WEIGHT:		**Not available**
VISCOSITY:		**2129 ± 495 mPa s**

@

F:	**68**
C:	**20**

SECTION 10: STABILITY AND REACTIVITY

STABILITY:

Stable under recommended storage conditions.

CONDITIONS TO AVOID (STABILITY):
Avoid moisture. Heat. Heat, flames and sparks. Extremes of temperature and direct sunlight.

INCOMPATIBILITY (MATERIAL TO AVOID):
Acids, bases and oxidizing agents

HAZARDOUS DECOMPOSITION OR BY-PRODUCTS:
Traces of hydrogen chloride, other decomposition products – no data available. In case of a fire, see section 5.

HAZARDOUS POLYMERIZATION:
Not determined.

CONDITIONS TO AVOID (POLYMERIZATION):
Not determined.

SECTION 11: TOXICOLOGICAL INFORMATION

TOXICOLOGICAL INFORMATION:
No data have been prepared.

Exposure to vapour from the organic solvents contained within the product (Tetrahydrofuran, Methyl Ethyl Ketone) above the noted exposure limits may lead to irritation of the mucous membranes of the upper respiratory tract which may lead to harmful effects for health. Exposure to high concentrations of solvent vapour may cause cough, nausea and vomiting including neurological symptoms (debilitation, intoxication and loss of conscience). Prolonged or repeated exposure can cause nausea, headache, vomiting and narcosis. Contact with eyes and skin may lead to irritation.

SECTION 12: ECOLOGICAL INFORMATION

ECOLOGICAL INFORMATION:
No data have been prepared.

The product contains substances that may present a danger for the environment during spillage – accidental or deliberate. Do not let product enter drains.

SECTION 13: DISPOSAL CONSIDERATIONS

WASTE DISPOSAL METHOD:
Do not pour into sewers or into rivers, streams or canals.
Waste and used packing must be disposed in accordance with local authority requirements, such as through burning in a chemical incinerator equipped with an afterburner and scrubber, but exert extra care in igniting as this material is highly flammable.
The polluted packing should be emptied in an optimum manner so that it may be re-used after appropriate cleaning; surplus and non-recyclable product should be offered to a licenced disposal company. Contaminated packaging should be disposed as unused product.

RCRA HAZARD CLASS:
Not determined

SECTION 14: TRANSPORT INFORMATION

Transport the product in accordance with the regulations for dangerous goods authorized for road, rail, air and sea transport.

PROPER SHIPPING NAME:	Printing inks, flammable
HAZARD CLASS:	3
ID NUMBER:	N/A
PACKING GROUP:	II
LABEL STATEMENT:	Flammable

SECTION 15: REGULATORY INFORMATION

This safety datasheet complies with the requirements of Regulation (EC) No. 1907/2006.

SAFETY, HEALTH AND ENVIRONMENTAL REGULATIONS/LEGISLATION SPECIFIC FOR THE PRODUT:
No data available

CHEMICAL SAFETY ASSESSMENT:
For this product a chemical safety assessment was not carried out

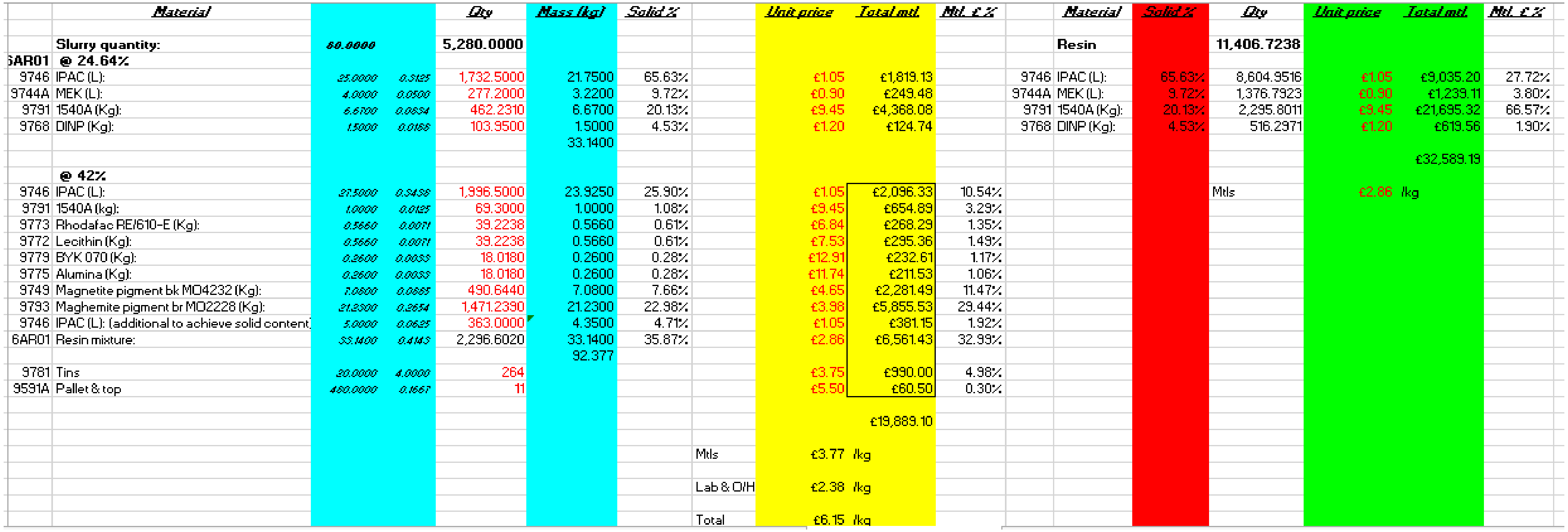
SECTION 16: OTHER INFORMATION

FULL TEXT OF H-STATEMENTS REFERRED TO UNDER SECTIONS 2 AND 3
EUH066 Repeated exposure may cause skin dryness or cracking.
Eye Irrit. Eye irritation
Flam. Liq. Flammable liquids
H225 Highly flammable liquid and vapour.
H319 Causes serious eye irritation.
H336 May cause drowsiness or dizziness.
STOT SE Specific target organ toxicity - single exposure

FULL TEXT OF R-PHRASES REFERRED TO UNDER SECTIONS 2 AND 3
F Highly flammable
Xi Irritant
R11 Highly flammable.
R36 Irritating to eyes.
R66 Repeated exposure may cause skin dryness or cracking.
R67 Vapours may cause drowsiness and dizziness.

Appendix 7: Example of Cost/kg for Magnetic Ink Production.

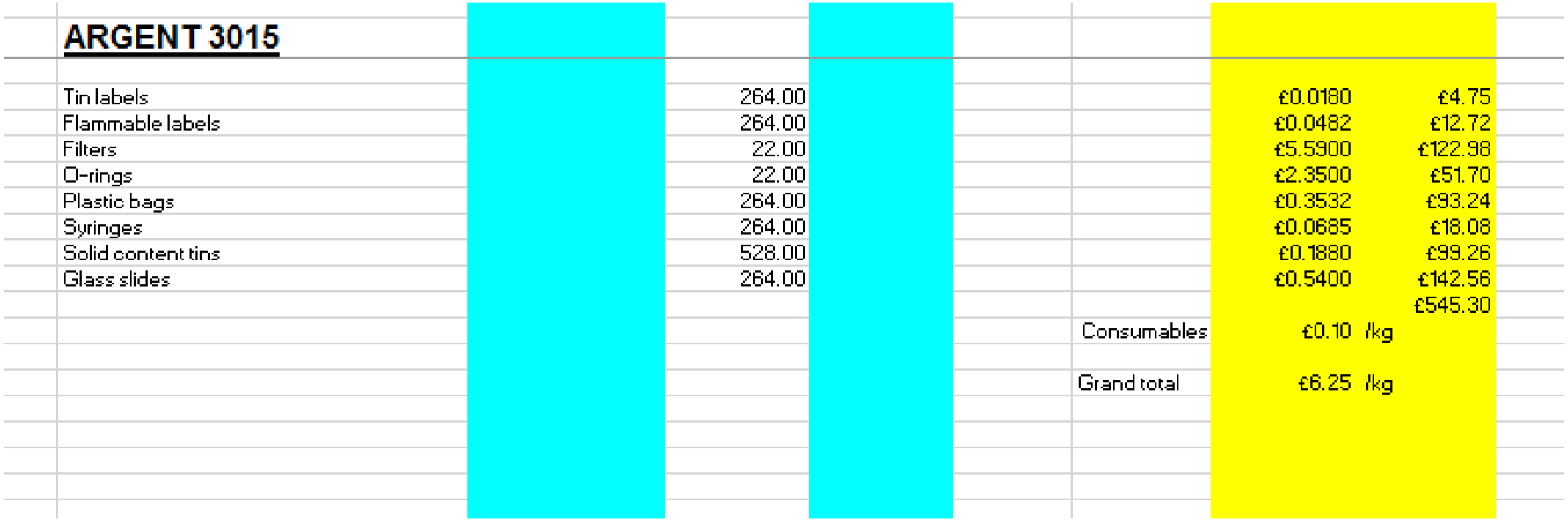
HL0104:



	Material			Qty	Mass (kg)	Solid %		Unit price	Total mtl.	Mtl £ %
	Slurry quantity:	80.0000		**5,280.0000**						
6AR01	**@ 24.64%**									
9746	IPAC (L):	25.0000	0.3125	1,732.5000	21.7500	65.63%		£1.05	£1,819.13	
9744A	MEK (L):	4.0000	0.0500	277.2000	3.2200	9.72%		£0.90	£249.48	
9791	1540A (Kg):	6.6700	0.0834	462.2310	6.6700	20.13%		£9.45	£4,368.08	
9768	DINP (Kg):	1.5000	0.0188	103.9500	1.5000	4.53%		£1.20	£124.74	
					33.1400					
	@ 42%									
9746	IPAC (L):	27.5000	0.3438	1,996.5000	23.9250	25.90%		£1.05	£2,096.33	10.54%
9791	1540A (kg):	1.0000	0.0125	69.3000	1.0000	1.08%		£9.45	£654.89	3.29%
9773	Rhodafac RE/610-E (Kg):	0.5660	0.0071	39.2238	0.5660	0.61%		£6.84	£268.29	1.35%
9772	Lecithin (Kg):	0.5660	0.0071	39.2238	0.5660	0.61%		£7.53	£295.36	1.49%
9779	BYK 070 (Kg):	0.2600	0.0033	18.0180	0.2600	0.28%		£12.91	£232.61	1.17%
9775	Alumina (Kg):	0.2600	0.0033	18.0180	0.2600	0.28%		£11.74	£211.53	1.06%
9749	Magnetite pigment bk MO4232 (Kg):	7.0800	0.0885	490.6440	7.0800	7.66%		£4.65	£2,281.49	11.47%
9793	Maghemite pigment br MO2228 (Kg):	21.2300	0.2654	1,471.2390	21.2300	22.98%		£3.98	£5,855.53	29.44%
9746	IPAC (L): (additional to achieve solid content)	5.0000	0.0625	363.0000	4.3500	4.71%		£1.05	£381.15	1.92%
6AR01	Resin mixture:	33.1400	0.4143	2,296.6020	33.1400	35.87%		£2.86	£6,561.43	32.99%
					92.377					
9781	Tins	20.0000	4.0000	264				£3.75	£990.00	4.98%
9591A	Pallet & top	480.0000	0.1667	11				£5.50	£60.50	0.30%
									£19,889.10	
							Mtls	£3.77	/kg	
							Lab & O/H	£2.38	/kg	
							Total	£6.15	/kg	

	Material	Solid %	Qty	Unit price	Total mtl.	Mtl £ %
	Resin		**11,406.7238**			
9746	IPAC (L):	65.63%	8,604.9516	£1.05	£9,035.20	27.72%
9744A	MEK (L):	9.72%	1,376.7923	£0.90	£1,239.11	3.80%
9791	1540A (Kg):	20.13%	2,295.8011	£9.45	£21,695.32	66.57%
9768	DINP (Kg):	4.53%	516.2971	£1.20	£619.56	1.90%
					£32,589.19	
			Mtls	£2.86	/kg	

(Continued on next page for total).



ARGENT 3015

Tin labels	264.00		£0.0180		£4.75
Flammable labels	264.00		£0.0482		£12.72
Filters	22.00		£5.5900		£122.98
O-rings	22.00		£2.3500		£51.70
Plastic bags	264.00		£0.3532		£93.24
Syringes	264.00		£0.0685		£18.08
Solid content tins	528.00		£0.1880		£99.26
Glass slides	264.00		£0.5400		£142.56
					£545.30
		Consumables	£0.10	/kg	
		Grand total	£6.25	/kg	

Appendix 8: Risk Log and Analyses

Resources Risk

Risk1: BH Looper currently employed is old, and may breakdown.

Response: UoH was planning to purchase a BH looper system (cost US$1250.00) as a back-up, however further information has identified that this system is not suitable for the full range of slurries that are needed for manufacture. A back-up system is the MOKE offered by Hinds Instruments, as indicated at LMC03 (cost ~£30k)

Risk2: Strontium ferrite cannot be sourced

Response: Current trials for HH0303 identify that only the squareness parameter is out of specification; a road-map to overcome this has been identified.

Risk3: Inability to incorporate QMS totally

Response: Within the framework of BS EN ISO 9001:2008, senior management is required to provide resources to implement QMS to the required standard, this includes personnel and equipment costs.

Forward Supply Chain Risk (Counterparty Risk)

Risk: PID is unable to continue to use BBP manufactured slurries.

Response: BBP/HMI/PID are all collaborating closely together to overcome any issues associated with non-conformed slurry.

Foreign Currency Exchange Risk

Risk: Pigment and other raw material supplies are from outside the UK. The major customer (other than BBP) is PID who deal in Euros rather than Pounds Sterling. Other customers may have currencies that are unstable and prone to fluctuate wildly; this gives rise to significant foreign currency exchange risk.

Response: BBP needs to ensure that at all times, the financial assets denominated in a particular currency match the financial liabilities denominated within the same currency. Where product is purchased and sold in the same currency, no foreign exchange exposure exists. Where purchases and sales are priced in different currencies, BBP may need to buy or sell currency to balance the assets and liabilities by currency, thus eliminating this transactional foreign exchange risk. A further control that could be implemented is the monthly preparation of balance sheets for each of the major currencies, with any surplus assets or liabilities hedged as appropriate. This in itself may require significant development of internal control processes, hedging mechanism and IT systems including ever more automation of price and risk-related processes such as customer invoicing.

Appendix 9: Matlab Script File

```
%VSM5 - A script file to
analyse VSM data and report
Hc, Sq, SFD and error
%File written by Haydn Ward.
Last modified November 28,
2014.
%Modification for Vladimir's
data
%-----------------------------
----------------------------
%tolerance changed for this
PID version that is hand-
extrapolated
%tolerance should be 3e-4
%line 140 and 175 + or -
0.01e-4 not as 0.01 only...

%Clear all previous variables
clear
%Specify the file to read
filename='haydnPID.csv';

%Import the data, and assign
x and y values
haydn=importdata(filename);
[m,n]=size(haydn);
if rem(m,2)~=0; s=(m+1)/2;
else; s=m/2; end
x=haydn;
x(:,2)=[];
y=haydn;
y(:,1)=[];



%Smooth the data through
averaging over "smooth"
points
smooth=1;
num=round((m-smooth)/smooth);

kont=0;
for dummy=1:num;
kont=kont+1;
ax=x(1+(kont-
1)*smooth:kont*smooth);
realax(dummy)=mean(ax);
ay=y(1+(kont-
1)*smooth:kont*smooth);
realay(dummy)=mean(ay);
end

realax=reshape(realax,num,1);
realay=reshape(realay,num,1);
```

```
%Do the conversion into Oe
units
if max(realax)<1000;
realax=(realax*21021.0221)-
103.077;
end


%Centre the x-y plot
offsetx=max(realax)+min(reala
x);
ifoffsetx>0; xcorr=realax-
(offsetx/2); else;
xcorr=realax+(offsetx/2); end
offsety=max(realay)+min(reala
y);
ifoffsety>0; ycorr=realay-
(offsety/2); else;
ycorr=realay+(offsety/2); end


%Split data into forward
(demagnetisation) and
backward (magnetisation)
[m,n]=size(realax);
if rem(m,2)~=0; s=(m+1)/2;
else; s=m/2; end
xcorrf=realax(1:s);
xcorrb=realax(s+1:m);
ycorrf=realay(1:s);
ycorrb=realay(s+1:m);


%Determine the coercivity
from the experimental data
%Forward curve
%First do cubic spline
interpolation to increase the
data points near Hc
%Use 20000 interpolated
points
xif=linspace(-
1000,1000,20000);  %Generates
the points in the range to
interpolate
xif=reshape(xif,20000,1);
%This converts the row vector
to column vector
yif=spline(xcorrf,ycorrf,xif)
;  %This is the interpolation
```

```
step
%Work out values for when
ycorrf=0
%set tolerance as 3e-4
tol=500;
for k=1:20000;if
((yif(k,1)>=-
tol)&(yif(k,1)<=tol));hcmf(k,
1)=xif(k,1);end;end
[a,b]=size(hcmf);
%Now work out where the
matrix is filled so that mean
of the data can be
%obtained
count=0;
for
k=1:a;ifhcmf(k,1)~=0;count=co
unt+1;end;end
c=sum(hcmf);
hcf=round(c/count);
%Reverse curve
%First do cubic spline
interpolation to increase the
data points near Hc
%Use 20000 interpolated
points
xib=linspace(-
1000,1000,20000);  %Generates
the points in the range to
interpolate
xib=reshape(xib,20000,1);
%This converts the row vector
to column vector
yib=spline(xcorrb,ycorrb,xib)
;  %This is the interpolation
step



%Work out values for when
ycorrf=0
%keep tolerance as for
forward curve
for k=1:20000;if
((yib(k,1)>=-
tol)&(yib(k,1)<=tol));hcmb(k,
1)=xib(k,1);end;end
[d,e]=size(hcmb);
%Now work out where the
matrix is filled so that mean
of the data can be
%obtained
count=0;
for
k=1:d;ifhcmb(k,1)~=0;count=co
unt+1;end;end
f=sum(hcmb);
hcb=round(f/count);
%Calculate Hc according to
ISO/IEC 15457-2:2007, Annex A
hc=(hcb-hcf)/2;
```

```
%Determine the squareness
from the experimental data
[z,o]=size(xcorrf);
for k=1:z;
ifxcorrf(k,1)>1000;
part(k,1)=ycorrf(k,1);end;
end
[zaa,obb]=size(part);
top=sum(part)/zaa;


sqf=spline(xcorrf,ycorrf,0)/m
ax(ycorrf);
sqb=spline(xcorrb,ycorrb,0)/m
in(ycorrb);
sqav=(sqf+sqb)/2;
%Calculate Sq according to
ISO/IEC 15457-2:2007, Annex A
sq=sqf;
sq=spline(xcorrf,ycorrf,0)/to
p;
%Error in squareness
err_sq=abs(sqf-sqb);

%Determine the switching
field distribution
%Forward Curve
%Differentiate the curve
dydxf =
diff(ycorrf(:))./diff(xcorrf(
:));
ex=xcorrf;
ex(1,:)=[];

%Cubic spline interpolation
of differential
exs=xif;
exs(1,:)=[];
magf=spline(ex,dydxf,exs);
[g,h]=size(magf);
mexyf=max(magf);
%Determine internal error in
Hc - Hc should be value of x
when magf is max
for k=1:g;ifmagf(k,1)==mexyf;
hcfd=exs(k,1); end; end
hcfd=round(hcfd);
err_hcf=hcfd-hcf;
%Work out when differentiated
curve is at half-maximum h1
and h2
p=(mexyf/2)-0.005;
q=(mexyf/2)+0.005;
%Do calculation for h1
for k=1:g; if
(magf(k,1)>=p)&(magf(k,1)<=q)
&(exs(k,1)<hcf);honef(k,1)=ex
s(k,1); end;end
[l,r]=size(honef);
```

```
count=0;
for
k=1:l;ifhonef(k,1)~=0;count=c
ount+1;end;end
h1f=sum(honef)/count;
%Do calculation for h2
for k=1:g; if
(magf(k,1)>=p)&(magf(k,1)<=q)
&(exs(k,1)>hcf);htwof(k,1)=ex
s(k,1); end;end
[l,r]=size(htwof);
count=0;
for
k=1:l;ifhtwof(k,1)~=0;count=c
ount+1;end;end
h2f=sum(htwof)/count;
%Calculate SFD
sfdf=2*(h1f-h2f)/(h1f+h2f);
%Reverse Curve
%Differentiate the curve
dydxb =
diff(ycorrb(:))./diff(xcorrb(
:));
ex=xcorrb;
ex(1,:)=[];

%Cubic spline interpolation
of differential
exs=xib;
exs(1,:)=[];
magb=spline(ex,dydxb,exs);
[g,h]=size(magb);
mexyb=max(magb);

%Determine internal error in
Hc: Hc should be value of x
when magb is max
for k=1:g;ifmagb(k,1)==mexyb;
hcbd=exs(k,1); end; end
hcbd=round(hcbd);
err_hcb=hcbd-hcb;
err_hc=max(err_hcf,err_hcb);
%Work out when differentiated
curve is at half-maximum h1
and h2
p=(mexyb/2)-0.005;
q=(mexyb/2)+0.005;
%Do calculation for h1
for k=1:g; if
((magb(k,1)>=p)&(magb(k,1)<=q
)&(exs(k,1)<hcb));honeb(k,1)=
exs(k,1); end;end
[l,r]=size(honeb);
count=0;
for
k=1:l;ifhoneb(k,1)~=0;count=c
ount+1;end;end
h1b=sum(honeb)/count;
%Do calculation for h2
for k=1:g; if
(magb(k,1)>=p)&(magb(k,1)<=q)
&(exs(k,1)>hcb);htwob(k,1)=ex
s(k,1); end;end
[l,r]=size(htwob);
count=0;
for
k=1:l;ifhtwob(k,1)~=0;count=c
ount+1;end;end
h2b=sum(htwob)/count;
%Calculate SFD
sfdb=2*(h2b-h1b)/(h1b+h2b);
%Calculate SFD according to
ISO/IEC 15457-2:2007, Annex A
sfd=sfdb;
%Determine error in sfd
sfdav=.5*(sfdf+sfdb);
err_sfd=abs(sfdf-sfdb);

%Plot data graphs......
subplot(1,2,1)    %divide the
window into two half and plot
in first half
%Plot real and interpolated
points on graph;  centred
real as circles
plot(xif,yif,xib,yib,xcorrf,y
corrf,'o',xcorrb,ycorrb,'o')
xlabel('Applied
field/Oe'),ylabel('Magnetisat
ion/a.u.')
title('Hysteresis Loop')
legend('demagnetisation
interpolated data (cubic
spline)','magnetisation
interpolated data (cubic
spline)','experimental
demagnetisation','experimenta
l magnetisation')
subplot(1,2,2)     %get
second subwindow ready
%Plot the reverse sweep with
interpolated points
plot(exs,magb,ex,dydxb,'o')
xlabel('Applied
field/Oe'),ylabel('dM/dH')
title('Differentiated
Magnetisation Curve')


%Display the results of the
calculations with error
disp('VSM Data Analysis')
disp('In accordance with
ISO/IEC 15457-2:2007, Annex
A')
disp('-----------------------
-------------------------')
disp('  ')
disp(filename)
disp('  ')
disp('Data smoothed
over');disp(smooth);disp('poi
```

```
nts')
disp('***********************
*************************')
disp(' ')
disp('Coercivity:
'),disp(hc),disp(' +/-
'),disp(err_hc),disp(' Oe')
disp(' ')
disp('Expected value is 315
+/- 25 Oe for A3015')
disp('   ')
disp('***********************
*************************')
disp(' ')
disp('Squareness:
'),disp(sq),disp(' +/-
'),disp(err_sq)
disp(' ')
disp('Expected value is >=
0.7 for A3015')
disp('   ')
disp('The magnetisation value
depends strongly on the value
of the maximum applied
field.')
disp('Maximum field applied
was:
'),disp(max(xcorrf)),disp('
Oe')
disp('The accuracy of
squareness measurements is
dependent on the ability to
set the maximum applied field
to a reproducible value')
disp(' ')
disp('***********************
**************************')
disp(' ')
disp('Switching field
distribution:
'),disp(sfd),disp('+/-
'),disp(err_sfd)
disp('  ')
disp('Expected value is <=
0.7 for A3015')
disp('The measurement of SFD
is particularly vulnerable to
errors arising from small
changs on the M=f(H) curve,
as it uses a derivative
relation')
disp(' ')
disp('-----------------------
---------------------------')
```

The code produced the following data output.

```
VSM Data Analysis
In accordance with ISO/IEC 15457-2:2007, Annex A
---------------------------------------------

haydnPID.csv

Data smoothed over
     1

points
**********************************************

Coercivity:
   347

Oe

Expected value is 315 +/- 25 Oe for A3015

**********************************************

Squareness:
    0.7647


Expected value is >= 0.7 for A3015

The magnetisation value depends strongly on the value of the maximum
applied field.
Maximum field applied was:
   1.5176e+03

Oe
The accuracy of squareness measurements is dependent on the ability to set
the maximum applied field to a reproducible value

***********************************************

Switching field distribution:
    0.4271

Expected value is <= 0.7 for A3015
The measurement of SFD is particularly vulnerable to errors arising from
small changes on the M=f(H) curve, as it uses a derivative relation

-----------------------------------------------
```

Appendix 10: Matlab Code for the Evaporation of a Liquid from a Circular Disc

```
%evaporation.m
%Simulation of evaporating liquids/slurries
%Expanding time grid
clear
haydn=cputime;

%Index parameters
CH=100;
NT=500000;

%Cell parameters
relec    = 1e-2;
diffa=24.2e-6;
diffaz=diffa;
rat=diffaz/diffa;

Ao=2;

%Simulation length (s)
%tau=4.11;
tau=100;
simt=tau*relec*relec/4/diffa;
disp(sprintf('Transient for %f seconds',simt))

ala=20;
bee=1+2/ala/(tau^.5)/(rat^.25);
%bee=1;

%Mesh spacing
h=1/CH;

%Grid constants
%dt=tau/NT;
%Temporal grid needs to expand, so change from tao to omega
tao=0.025;
dto=tau/NT;
mo=1+(tao/dto);
omeg=5e-5; %omeg=0 corresponds to uniform time grid

dx=h;
dy=h;
%lambda=dt/4/h/h;


    for k=1:CH;
        theta(k)=k*dx;
    end

     for j=1:CH;
        gamma(j)=j*dy;
     end


      for k=1:CH;
```

```
      for j=1:CH;


LAMzz(j,k)=bee*bee*cos(pi*gamma(j)/2/bee)*cos(pi*gamma(j)/2/bee)/
pi/pi/((theta(k)*theta(k))+(tan(pi*gamma(j)/2/bee)*tan(pi*gamma(j
)/2/bee)));

      LAMrr(j,k)=(1-
(theta(k)*theta(k)))/4/((theta(k)*theta(k))+(tan(pi*gamma(j)/2/be
e)*tan(pi*gamma(j)/2/bee)));

      LAMr(j,k)=-
1*theta(k)/2/((theta(k)*theta(k))+(tan(pi*gamma(j)/2/bee)*tan(pi*
gamma(j)/2/bee)));

      end

      end

%  Initial Condiitons TIME = 0   *
      for k = 1:CH;
       for j = 1:CH;

        u(j,k)  = 0;
        oldu(j,k)  = 0;
        newu(j,k)  = 0;

       end
      end




%%%%%%%%%%%%%
%           %
% TIME LOOP %
%           %
%%%%%%%%%%%%%


      %for n = 1:NT;

      t=0;
      n=0;

      while (t<=tau);
          n=n+1;

          if (t<=tao);
              m=mo;
              dt=dto;
          else
              m=m+1;
              dt=dto*((1+omeg)^(m-mo));
          end

        curr(n) = 0.00;
        t=t+dt/2;
```

```
%%%%%%%%%%
% j loop %
%%%%%%%%%%
        uok=1;
        for j=1:CH-1;

%  Define Values for Algorithm
        k=1;
        if (j==1);
        d(1,1)=(LAMzz(1,1)*dt/2/h/h)*(oldu(2,1)+uok)+(1-
LAMzz(1,1)*dt/h/h)*oldu(1,1); %This one has aok present as uok
        elseif (j==CH-1);
        d(CH-1,1)=(LAMzz(CH-1,1)*dt/2/h/h)*(1+oldu(CH-2,1))+(1-
LAMzz(CH-1,1)*dt/h/h)*oldu(CH-1,1);
        else
        d(j,1) = (LAMzz(j,1)*dt/2/h/h)*(oldu(j+1,1)+oldu(j-
1,1))+(1-LAMzz(j,1)*dt/h/h)*oldu(j,k);
        end

        c(j,1)=-1*(dt/2/h)*(LAMrr(j,1)/h+LAMr(j,1)/2);
        b(j,1)=1+LAMrr(j,1)*dt/h/h/2+LAMr(j,1)*dt/4/h;
        a(j,1)=0.00;

        for k=2:CH-2;
        if (j==1);
        d(1,k)=(LAMzz(1,k)*dt/2/h/h)*(oldu(2,k)+uok)+(1-
LAMzz(1,k)*dt/h/h)*oldu(1,k);%This one has aok present as uok
        elseif (j==CH-1);
        d(CH-1,k)=(LAMzz(CH-1,k)*dt/2/h/h)*(1+oldu(CH-2,k))+(1-
LAMzz(CH-1,k)*dt/h/h)*oldu(CH-1,k);
        else
        d(j,k) = (LAMzz(j,k)*dt/2/h/h)*(oldu(j+1,k)+oldu(j-
1,k))+(1-LAMzz(j,k)*dt/h/h)*oldu(j,k);
        end

        c(j,k)=-1*(dt/2/h)*(LAMrr(j,k)/h+LAMr(j,k)/2);
        b(j,k)=1+LAMrr(j,k)*dt/h/h;
        a(j,k)=-1*(dt/2/h)*(LAMrr(j,k)/h-LAMr(j,k)/2);

        end

        k=CH-1;
        if (j==1);
        d(1,CH-1)=(LAMzz(1,CH-1)*dt/2/h/h)*(oldu(2,CH-
1)+uok)+(1.-LAMzz(1,CH-1)*dt/h/h)*oldu(1,CH-1);%This one has aok
present as uok
        elseif (j==CH-1);
        d(CH-1,CH-1)=(LAMzz(CH-1,CH-1)*dt/2/h/h)*(1.+oldu(CH-
2,CH-1))+(1-LAMzz(CH-1,CH-1)*dt/h/h)*oldu(CH-1,CH-1);
        else
        d(j,CH-1) = (LAMzz(j,CH-1)*dt/2/h/h)*(oldu(j+1,CH-
1)+oldu(j-1,CH-1))+(1-LAMzz(j,CH-1)*dt/h/h)*oldu(j,CH-1);
        end

        c(j,CH-1)=0.00;
        b(j,CH-1)=1+LAMrr(j,CH-1)*dt/2/h/h-LAMr(j,CH-1)*dt/4/h;
        a(j,CH-1)=-1*(dt/2/h)*(LAMrr(j,CH-1)/h-LAMr(j,CH-1)/2);
```

```
%  Thomas Algorithm
        alpha(j,1)  = b(j,1);
        beta(j,1)  = c(j,1)/alpha(j,1);

        for k=2:CH-1;
        alpha(j,k)=b(j,k)-a(j,k)*beta(j,k-1);
        beta(j,k)  = c(j,k)/alpha(j,k);
        end

        f(j,1)  = d(j,1)/alpha(j,1);

        for k=2:CH-1;
          f(j,k)  = (d(j,k)-a(j,k)*f(j,k-1))/alpha(j,k);
        end

        u(j,CH-1)  = f(j,CH-1);

        for k=CH-2:-1:1;
          u(j,k)  = f(j,k)-beta(j,k)*u(j,k+1);
        end

        end
% j loop ended

%  Store Concentration Profiles for next time step

        for k=1:CH;
         for j=1:CH;
          newu(j,k)  = u(j,k);
         end
        end

%%%%%%%%%%
% k loop %
%%%%%%%%%%

         t=t+dt/2;

        for k=1:CH-1;

%  Define Values for Algorithm
        j=1;%This one has aok present as uok in d(j) etc.
        if (k==1) ;
        d(1,1)=(dt/2/h)*(LAMrr(1,1)/h+LAMr(1,1)/2)*newu(1,2)+(1-
LAMrr(1,1)*dt/2/h/h-
LAMr(1,1)*dt/4/h)*newu(1,1)+LAMzz(1,k)*dt*uok/2/h/h;
        elseif (k==CH-1);
        d(1,CH-1)=(1.-LAMrr(1,CH-1)*dt/2/h/h+LAMr(1,CH-
1)*dt/4/h)*newu(1,CH-1)+(dt/2/h)*(LAMrr(1,CH-1)/h-LAMr(1,CH-
1)/2)*newu(1,CH-2)+LAMzz(1,k)*dt*uok/2/h/h;
        else
        d(1,k)  =
(dt/2/h)*(LAMrr(1,k)/h+LAMr(1,k)/2)*newu(1,k+1)+(1-
LAMrr(1,k)*dt/h/h)*newu(1,k)+(dt/2/h)*(LAMrr(1,k)/h-
LAMr(1,k)/2)*newu(1,k-1)+LAMzz(1,k)*dt*uok/2/h/h;
        end
```

```
        c(1,k)=-1*LAMzz(1,k)*dt/2/h/h;
        b(1,k)=1+LAMzz(1,k)*dt/h/h;
        a(1,k)=0.00;

        for j=2:CH-2;

        if (k==1) ;
        d(j,1)=(dt/2/h)*(LAMrr(j,1)/h+LAMr(j,1)/2)*newu(j,2)+(1-
LAMrr(j,1)*dt/2/h/h-LAMr(j,1)*dt/4/h)*newu(j,1);
        elseif (k==CH-1);
        d(j,CH-1)=(1-LAMrr(j,CH-1)*dt/2/h/h+LAMr(j,CH-
1)*dt/4/h)*newu(j,CH-1)+(dt/2/h)*(LAMrr(j,CH-1)/h-LAMr(j,CH-
1)/2)*newu(j,CH-2);
        else
        d(j,k) =
(dt/2/h)*(LAMrr(j,k)/h+LAMr(j,k)/2)*newu(j,k+1)+(1-
LAMrr(j,k)*dt/h/h)*newu(j,k)+(dt/2/h)*(LAMrr(j,k)/h-
LAMr(j,k)/2)*newu(j,k-1);
        end

        c(j,k)=-1.*LAMzz(j,k)*dt/2/h/h;
        b(j,k)=1+LAMzz(j,k)*dt/h/h;
        a(j,k)=-1*LAMzz(j,k)*dt/2/h/h;

        end

        j=CH-1  ;
        if (k==1);
        d(CH-1,1)=(dt/2/h)*(LAMrr(CH-1,1)/h+LAMr(CH-
1,1)/2)*newu(CH-1,2)+(1-LAMrr(CH-1,1)*dt/2/h/h-LAMr(CH-
1,1)*dt/4/h)*newu(CH-1,1)+LAMzz(CH-1,1)*dt/2/h/h;
        elseif (k==CH-1);
        d(CH-1,CH-1)=(1-LAMrr(CH-1,CH-1)*dt/2/h/h+LAMr(CH-1,CH-
1)*dt/4/h)*newu(CH-1,CH-1)+(dt/2/h)*(LAMrr(CH-1,CH-1)/h-LAMr(CH-
1,CH-1)/2)*newu(CH-1,CH-2)+LAMzz(CH-1,CH-1)*dt/2/h/h;
        else
        func=LAMzz(CH-1,k)*dt/2/h/h;
        d(CH-1,k) = (dt/2/h)*(LAMrr(CH-1,k)/h+LAMr(CH-
1,k)/2)*newu(CH-1,k+1)+(1-LAMrr(CH-1,k)*dt/h/h)*newu(CH-
1,k)+(dt/2/h)*(LAMrr(CH-1,k)/h-LAMr(CH-1,k)/2)*newu(CH-1,k-
1)+func;
        end

        c(CH-1,k)=0.00;
        b(CH-1,k)=1+LAMzz(CH-1,k)*dt/h/h;
        a(CH-1,k)=-1*LAMzz(CH-1,k)*dt/2/h/h;


%  Thomas Algorithm
        alpha(1,k) = b(1,k);
        beta(1,k) = c(1,k)/alpha(1,k);

       for j=2:CH-1;
        alpha(j,k)=b(j,k)-a(j,k)*beta(j-1,k);
        beta(j,k) = c(j,k)/alpha(j,k);
       end

        f(1,k) = d(1,k)/alpha(1,k);
```

```
        for j=2:CH-1;
          f(j,k) = (d(j,k)-a(j,k)*f(j-1,k))/alpha(j,k);
        end

        u(CH-1,k) = f(CH-1,k);

        for j=CH-2:-1:1;
          u(j,k) = f(j,k)-beta(j,k)*u(j+1,k);
        end

      end
% k loop ended

%  Store Concentration Profiles for next time step

        for k=1:CH;
         for j=1:CH;
          oldu(j,k) = u(j,k);
%          u(j,k) = 0.00
         end
        end


% Calculate Currents using Trapezoidal Quadrature

       for k=1:CH-1;
%         curr(n) = curr(n)+u(1,k)

        if (k==1) ;
            curr(n)=1.5*(oldu(1,1)-uok);
        elseif  (k==CH-1);
          curr(n)=curr(n)+1.5*(oldu(1,CH-1)-uok);
        else
          curr(n) = curr(n)+(oldu(1,k)-uok);
        end
       end

       inorm(n)=-bee*curr(n)*dx/dy;



       %tamp(n)=n*dt;
       tamp(n)=t;

       %shoup-szabo
       ss(n)=.7854+.25*sqrt(pi/(tamp(n)/4))+.2146*exp(-
.3912/sqrt(tamp(n)/4));

       disp(sprintf('%f % completed',100*t/tau))

      end
      disp(sprintf('Simulation has taken %f seconds',cputime-
haydn))

plot(log10(tamp),log10(ss),'ro',log10(tamp),log10(inorm),'linewid
th',2)
```