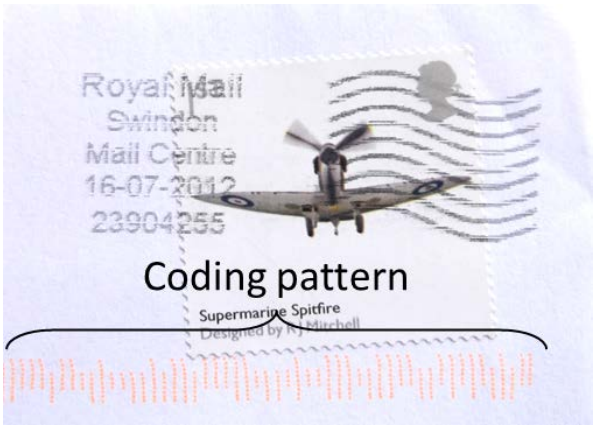
Institution: Lancaster University

Unit of Assessment: 8 Chemistry

Title of case study: Luminescent inks for mail coding and sorting

1. Summary of the impact



Fundamental research in collaboration with Royal Mail into luminescence molecules constrained within a water-soluble acrylic polymer matrix has led to the development of novel, water-soluble, ink-jet printable, luminescent inks. These inks are employed by Royal Mail for printing coding patterns on envelopes that can be read by automatic letter-sorting machines. The inks offer excellent performance in humid environments, on coloured paper, and on paper containing optical brighteners, and are safer. Royal Mail delivers, on average, 58 million letters each day, representing annual revenue of £5.2 billion. The research at Lancaster enabling the innovation has a direct impact on the commercial performance of Royal Mail, the safety of its employees and the public, and everyone (commercially and/or privately) using Royal Mail services to send and receive mail correctly, quickly, and at a low cost.

2. Underpinning research

In 1987, Dr A. R. "Tim" Lane, a Senior Scientist at the Royal Mail Research Laboratories, approached Dr John Ebdon, Senior Lecturer, Chemistry Department, Lancaster University, for help in improving the physical and chemical properties of ink-jet printable inks used for printing machine-readable patterns of dots (representing postal codes) on envelopes, enabling the envelopes to be automatically sorted. At the time, the inks already in use for this purpose were based on suspensions of relatively simple phosphors in aqueous solutions of amino resins. These inks were believed first to dry and then to cure (crosslink) when applied to paper, providing a solid hydrophobic medium in which phosphorescence could develop and be "read" when the envelope was passed under a UV lamp. There were three problems with the inks: (1) the inks contained small amounts of free formaldehyde (a suspected carcinogen); (2) they were slow to dry/cure, leading to an unacceptable delay before the coding pattern could be read, and (3) they performed poorly in humid environments.

The academic outcomes of the project are described in five papers published jointly by Royal Mail and Lancaster University over the period 1995-1999 [1-5]. These demonstrate: (1) that water-soluble acrylic polymer solutions, e.g. aqueous solutions of polyacrylic and polymethacrylic acids, during the process of drying undergo a "coil-collapse" process whereby the interiors of the polymer coils become sufficiently hydrophobic to act as hosts for hydrophobic, luminescent materials (guests); (2) that in these collapsed coils, luminescence of the guest can occur without significant quenching, even before the solution has fully dried; (3) that the onset of coil-collapse is influenced by temperature and pH; and (4) that the hydrophobicity of the collapsed coil can be increased by the incorporation of small amounts of a hydrophobic monomer, such as styrene or methyl methacrylate. A further outcome, not published at the time owing to commercial sensitivity, was the demonstration that a bi-component luminescent system in a polymer matrix, in which energy transfer to a fluorescent compound occurs, could be used to give *long-lived red* luminescence.

The fundamental research on the behaviours of water-based polymer systems carried out at

Lancaster, and the more applied aspects researched jointly by Lancaster and Royal Mail, led to the patenting of polyacrylic acid binders together with various combinations of luminescent compounds for use in mail coding inks, by Royal Mail in 1998 [6]. These patents refer to the environmental hazards posed by the earlier amino resin binders and for the desirability that the ink should contain a long-lived *red emitter* so as to allow signals to be read (a) irrespective of the substrate colour, (b) in the presence of a fluorescence background from any optical brighteners in the envelope paper, and (c) throughout the period during which the coding ink is drying. The use of energy transfer to achieve long-lived (>500 ms) luminescence is also disclosed.

3. References to the research

[1]. Ebdon J. R., Lane A. R., Lucas D. M., Soutar, I. and Swanson L. (1995) *Luminescence studies of polymer matrices. 1. Phosphorescence of benzophenone dispersed in poly(methyl methacrylate)*, Polymer, **36**, 1577-1584. DOI: 10.1016/0032-3861(95)99002-C

[2]. Ebdon J. R., Hunt B. J., Lucas D. M., Soutar I., Swanson L. and Lane A. L. (1995) *Luminescence studies of hydrophobically modified, water-soluble polymers. 1. Fluorescence anisotropy and spectroscopic investigations of the conformational behaviour of copolymers of acrylic acid and styrene and methyl methacrylate*, Canadian Journal of Chemistry, **73**, 1982-1994. DOI: 10.1139/v95-245

[3]. Ebdon J. R., Soutar I., Brown P., McCabe A. J., Lane A. R. and Swanson L. (1999) *Luminescence studies of polymer matrices: 2. On the phosphorescence characteristics of 2-benzoyl naphthalene dispersed in various acrylic polymers*, High Perf. Polym., **11**, 49-62. DOI: 10.1088/0954-0083/11/1/005

[4]. Ebdon J. R., Soutar I., Brown P., McCabe A. J., Lane A. R. and Swanson L. (1999) *Luminescence studies of polymer matrices: III. Characterization and evaluation of acrylic acid based polymers as hosts for a phosphorescent coding system*, J. Polym. Sci. B. Polym. Phys. Ed., **37**, 2127-2136. DOI: 10.1002/(SICI)1099-0488(19990815)37:16

[5]. Ebdon J. R., Lane A. R., Lucas D. M., Soutar I. and Swanson L. (1999) *Luminescence studies of polymer matrices. 4. Phosphorescence of benzophenone dispersed in acrylic acid based polymer films*, High Perf. Polym., **11**, 331-341. DOI: 10.1088/0954-0083/11/3/308

[6]. Brown P. R., Hewison S., Kondratowicz A., Metson C. A. L., Rock J. and Scott R. (1998) Patents WO19980003596 and EP 0914392B, assigned to the Post Office.

4. Details of the impact

The new ink formulations were introduced in the Royal Mail processes in 2006-7, defining the date of onset of impact.

Embedding of Technology: Key to the realisation of the impact of this research programme was the embedding of the technology developed at Lancaster University into Royal Mail Research Laboratories. Linda Swanson [1-5] was a PhD student on the programme, who was subsequently employed by Royal Mail for three years. Paul Brown and Alistair McCabe, employed at Royal Mail Research Laboratories, were members of the research team [1-5]. The research initiated through the partnership with Lancaster University was subsequently refined at Royal Mail Research Laboratories, which led to a further patent [7] where practical ink formulations are described which include the addition of an opacifying agent (to enhance the fluorescence signal on highly coloured envelopes and wrappings, and therefore enhancing the reliability of the automated barcode reading equipment). A further development was to incorporate dyes that could be monitored at two distinct excitation wavelengths (e.g. 365 nm and 420 nm) which can be 'read' using a combination

of UV and visible illumination. Such formulation is typical of what is used by Royal Mail to print digital postmarks (DPMs) as barcodes on letters and parcels.

The IMPACT is evident under THREE distinct headings:

SAFETY – The earlier formulations, based on formaldehyde (a suspected carcinogen), have been replaced by safer polyacrylic and later styrene-acrylic resins [7]. The principal impact is on the safety of Royal Mail workers who operate the barcoding printers where the risk of exposure to the wet inks is greatest. Other postal workers, such as postmen and women who are exposed to the cured inks throughout their daily employment, will not be subjected to persistent formaldehyde outgassing. Neither will the general public be exposed to formaldehyde. Safety, of paramount importance, is a significant impact that is directly related to the inks developed through the Lancaster University/Royal Mail partnership.

EFFICIENCY – Royal Mail is characterised by its massive daily throughput of letters and parcels (typically 58 million items per day [8]). The logistics can only be realised in a sensible and cost-effective way through the extensive application of intelligent automation. Fundamental to the automation of postal delivery is the ability to assign each postal item uniquely, and with sufficient data to ensure accurate delivery to the intended destination. The DPMs, as barcodes, are readable by intelligent letter sorting machines. Prior to 2006, most mail was still hand sorted, which is a "slow and cumbersome process" [8]. Royal Mail introduced a major modernisation programme in 2006-07, coincident with the updated coding ink formulation [7], [8]. During this modernisation programme, 64 intelligent letter sorting machines were installed, each capable of processing up to 40,000 items of mail per hour [7]. This has also led to the adoption of Compact Sequence Sorters that are "walk-sequenced", so that letters are ordered to minimise the travel distance by postmen and women. This now accounts for about 75% of all deliveries. This has the direct impact of reducing the workload of the delivery personnel, and thereby increasing efficiency of the delivery process. In turn, this efficiency improvement leads to a reduction in cost. During the year 2011-12, a total of 235 new, refurbished or upgraded process sequencing machines were installed across the UK Royal Mail network. The coding inks are pivotal to the IMPACT achieved in terms of postal delivery efficiency.

FINANCIAL – Royal Mail has been hit by a general decline in mail volumes within the last decade due to electronic substitution of paper communication (for example, Royal Mail observed a 3.1% pa decline in letter volumes between 2005 and 2008). For Royal Mail to remain competitive alongside the trend towards electronic communication, it has been essential to enhance their efficiency, as described above. This will continue to be an acute risk for Royal Mail, as they predict letters will decline 5% pa during the period 2013-18; and 4% pa during 2018-23 [9]. The UK market present and predicted volumes are: 2012 (Letters 13.8 billion; Parcels 1.7 billion); 2023 (Letters 8.3 billion; Parcels 2.3 billion) [9]. Recent (2011) revenue figures for Royal Mail are £5.2 billion pa [8]. This is a significant business in its own right that is dependant for efficiency upon the coded inks developed from the expertise at the University of Lancaster. From a societal standpoint, the IMPACT is far greater, since the mail volume accounts for vital communications within both the domestic and business sectors, with a predicted volume in excess of 10 billion items pa up to 2023, even in the light of the trend towards electronic communication. The recent flotation of Royal Mail, the oversubscription of prospective shareholders, and the rapid increase of share value by 48% [10] is clear evidence of a flourishing business with a strong future prospect. The IMPACT of the coding inks has played a significant part in the success of Royal Mail through the facilitation of considerable efficiency gains through intelligent automation. This is IMPACT that is set to continue to deliver for the foreseeable future [9].

With respect to corroboration, we quote below from a correspondence [11] with Linda Swanson who contributed to the fundamental research as a PhD student but then went onto work for Royal Mail and played a key role in embedding the printing inks science and technology within Royal Mail. She is therefore well placed to corroborate the implementation of the technology within Royal Mail.

'the most important and tangible output from this work is the red ink which currently appears on letters coded by Royal Mail – this was the ink that was designed and developed at Lancaster during that project.'

5. Sources to corroborate the impact

[7]. GB 2412659 B, 2005, assigned to the Royal Mail
[8]. Royal Mail Holdings plc, Annual Report and Financial Statements, 2011-2012.
[9]. PwC Strategy & Economics, "The outlook for UK mail volumes to 2023", PWC July 2013.
[10]. http://www.thisismoney.co.uk/money/news/article-2458523/Royal-Mail-shares-surge-stand-48-float-price.html [accessed 5 Nov 2013]
[11] Correspondence with respect to the project from a former Royal Mail employee associated with embedding Lancaster's research within Royal Mail.

Contact 1: Royal Mail Group Dangerous Goods Advisor, Royal Mail Engineering – can corroborate implementation of printing inks technology within Royal Mail
Contact 2: Former Royal Mail employee (now at Sheffield University) – can corroborate the implementation of the technology