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Chris Taylor is a Fellow of the IVE with over 35 years enamelling experience and is a lecturer for the IVE Basic Approach Course.

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EDITORIAL – SPRING 2008

This is my first edition of ‘The Vitreous Enameller’ as Editor. As most of you will know, I take the reigns from John Mullis who has done a fine job compiling this journal for the last 15 years. I would like to thank John on behalf of the vitreous enamelling industry for his considerable contribution to our profession and wish him all the best with his future plans after retiring from Ferro in April of this year. John will continue to serve on the Council of the IVE and also as a member of BSI’s STI/36 committee.

--ooOoo--

The Institute is facing an increasingly challenging time. The number of companies enamelling in the UK is dwindling at an alarming rate and this in turn is having an impact on the support received by the Institute. Perhaps now is the time to take a good look at ourselves as an organisation and decide whether we should be adapting to the new environment we find ourselves in. Without doubt we need to continue to serve our existing members to ensure their continued support but the question is; should we be exploring new avenues that guarantee the existence of a professional body for enamellers in the UK?

The Institute is in need of ideas and suggestions and where better place to look for that input than from our members. How do you think the IVE could mould itself to ensure its future existence? Should we amalgamate with another institute within the UK? Should we extend the IVE’s links to the countries of Eastern Europe, where most of our industry appears to be heading? Perhaps the IVE could be used to open doors of opportunity for the industry that remains in the UK, forging links with the new enamelling regions? Does the Institute need to undergo a radical transformation to be more attractive to current non-members? If so, how should we do this? If you have an opinion, why not contact the IVE through the website; www.ive.org.uk. If you want your suggestion to remain anonymous, state this on your communication. We will publish any suggestions in the next edition of ‘The Vitreous Enameller.’ Unfortunately the IVE Yahoo Chat Group has been suspended for the time being but we can still use the journal to get a debate going on this issue.
The IVE has within its organisation a wealth of experience and is a source of information that is often undervalued and underused, even by its own members within the UK.

Another area where the Institute is seriously underused is that of enamelling industry representation on standards committees. I am fairly certain that many companies are unaware of the implications national, European and international standards can have on their business. There is a feature in ‘Standards News’ in this edition of the Vitreous Enameller, which I urge you to read.

As an organisation I believe we still have much to offer but it’s clear we need to think about the direction of the IVE as we enter into a new area of world enamelling.

MARK MORIARTY
Editor

--ooOoo--
INSTITUTE NEWS

We would like to welcome the following new Company Member:

Unique Enamelling Services Limited

Unit J, Bee Mill
Preston Road
Nr. Preston, Lancashire PR3 3XL

Company Representative: David Shaw

--ooOoo--

FORTHCOMING EVENTS

June 1st - 4th 2008
5th China International Steel Congress
- Green Steel.
Venue: Shanghai, China.
Contact: Ms. May Bai
T: 0086 10 65253774

June 2nd - 3rd 2008
1st National Meeting on Steelmaking.
Venue: Rio de Janeiro, Brazil.
T: (21) 2524 6917
Web: www.ibs.org.br/encontro
**THE VITREOUS ENAMELLER**

**June 3rd - 4th 2008**
SURFEX 2008.
Venue: Harrogate, UK.
Contact: Yvonne Waterman
T: +44 (0) 20 8908 1086
Web: www.surfex2008.net
Web: www.aimnet.it/eccc2008.htm

**June 2nd – 4th 2008**
IVE Technical Seminar 2008, including visit to Pfaudler Balfour, Leven, Fife, Scotland.
Contact: Angela Nutting
Tel: +44 (0) 1543 450596
Web: www.ive.org.uk

**June 3rd - 5th 2008**
Venue: Maastricht, Netherlands.
Contact: Bridget Brommer
T: +49 (0) 211 1591 303
Web: www.dvs-ev.de/itsc2008/

**June 3rd – 6th 2008**
American Coatings Show 2008.
Venue: Charlotte, USA.
Contact: Dirk Ebener
T: +1 (770) 618 58 30
Web: www.american-coatings-show.com

**June 16th – 17th 2008**
6th European Conference on Continuous Casting.
Venue: Riccione, Italy.
Contact: Association Italiana di Metallurgia (AIM)
T: +39 02 76021132
June 20th 2008
Venue: London, UK.
Contact: London Festival of Architecture
Tel: +44 (0) 20 7436 8625
Web: www.lfa2008.org/

June 29th – July 3rd 2008
Venue: Verona, Italy.
Contact: Agenza Polo Ceramico
T: +39 0546 670307
Web: www.icc2.org/

July 2nd 2008
Packaging Summit Europe 2008.
Venue: Amsterdam, Netherlands.
Contact: Chris White
T: +44 (0) 20 8846 2713
Web: www.pkeurope.com/

--ooOoo--
BUSINESS NEWS

COMPLIANCE MONITORING FOR THE VITREOUS ENAMEL INDUSTRY

Analytical Technology Inc. (ATi) announces that its diverse range of water monitors offers unique benefits for the vitreous enamel industry, enabling timely and cost-effective regulatory compliance. The treatment of effluent generated from vitreous enamel manufacturers in the UK is governed by strict regulations such as consent to discharge to public sewers, governed in the UK by the Environment Agency and by water companies. European consent conditions for discharge to controlled waters are becoming ever more stringent, with the risk of legal proceedings for continued consent failure. ATi’s monitors provide dependable and accurate results, helping manufacturers to easily and quickly comply with these rules.

Effluent treatment in the vitreous enamel industry often involves pH correction and reduction in the level of suspended solids. The control of the addition of acids and bases needs accurate, reliable measurement of pH in dirty and sometimes aggressive waste waters.

A typical process might be the use of acids to dissolve waste materials followed by the addition of e.g. sodium hydroxide and a ferric coagulant for precipitation. A simple flow through system consisting of several tanks with mixers and chemical dosing systems is often used. To optimise the chemistry pH must be maintained within fairly tight limits.

Continuous measurement of pH in such conditions is traditionally difficult as sensors quickly become fouled or poisoned. The Q series pH monitor with integral air cleaning allows reliable measurement of pH with minimal operator intervention and allows full automation of effluent treatment plants. The AutoClean system is programmable for 12 to 1 times per day and eliminates the need for costly and time consuming manual cleaning. Better control of the process will lead to better treatment and to reduced costs.

After treatment the waste water stream is returned to process or discharged to sewer or to a water course. If the water is discharged is at this point that pH
and suspended solids must often be measured to determine the compliance to EA or Water Company limits.

Turbidity/suspended solids measurement normally goes hand in hand with pH measurement as part of the discharge monitoring. Manual sampling can prove costly and does not give a full picture of the patterns of emissions. Sensor fouling can be a major problem with on line systems. ATi manufactures a suspended solids monitor with same AutoClean air blast system as the pH monitor. Turbidity is a general indicator of the optical clarity of water and is defined as the amount of light scattered from particles in solution. ATI’s D15/76 auto-clean turbidity monitor is designed to meet the needs of industrial water treatment for reliable, low-range turbidity measurements. With an air-blast cleaning system that automatically cleans the sensor as often as necessary, the D15/76 completely eliminates sensor fouling and maintains reliable measurements of turbidity in wastewater.

Michael Strahand
General Manager of Analytical Technology
T: +44 (0) 145 783 2800
Web: www.analyticaltechnology.com
IS THE LACK OF IVE, VEA AND IEI REPRESENTATION ON STANDARDS COMMITTEES A CAUSE FOR CONCERN FOR YOUR BUSINESS?

There are currently 1,350 BSI committees with approximately 10,000 members. All committee members give their time and expertise on a voluntary basis often with the support of their employer or trade association, although DTI funding is available for certain activities. The commitment required varies between and within committees, depending on the current work programme and the level of participation. Most committees only meet a few times each year but some members also represent the national view at European and international meetings abroad.

Although participation is voluntary, companies and individuals are likely to benefit from helping to develop standards since committee members can influence the content of standards; gain detailed advance knowledge of standards and so anticipate requirements and trends; get to know their peers and others who influence industry such as the business community, consumers, users, government and regulators. It’s possible to win recognition through association with leaders in the field and in media coverage promoting a standard and to be nominated for European or international committees.

It is a requirement of BSI’s bye-laws that all national committees are representative of the interests of users, manufacturers, government departments and other bodies concerned with their work. Companies do not generally nominate people directly to committees; trade associations or professional bodies such as the Institute of Vitreous Enamellers and the Vitreous Enamel Association are more frequently identified as nominating organisations, with the expertise to represent the best interests of their industry.
The list below details a number of committees that the IVE, VEA or IEI are recognised as a nominating organisation. It can be seen that with the exception of STI/36, the committee for vitreous enamel coatings, representation from the enamelling community is by and large quite poor. How many of these ‘unrepresented’ committees could potentially have an impact on your business? Representation on the relevant committee could not only keep you up to date with any important changes to standards you and your competitors are working to but also give you an opportunity to make sure your product is still compliant in revised editions of standards!

Personal and company membership to the Institute of Vitreous Enamellers is one way of making sure your business is represented on the appropriate committee. The IVE can nominate an expert on your behalf to sit on committees to represent your interests and report back on any developments. Alternatively, you may have a member of staff you feel has sufficient expertise to represent your company’s interests and that the IVE can nominate for committee membership.

If you are interested in more information on representation on standards committees, please contact the IVE through the website; www.ive.org.uk

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<td>B/549</td>
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<td>No representation</td>
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<td>Not aware of active representation</td>
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### Materials and Chemicals Committees

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<th>Reference</th>
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<td>STI/35</td>
<td>Design of articles to be coated</td>
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<td>CEN/TC164/WG3</td>
<td>Water supply – influence of materials on water intended for human consumption – influence due to migration</td>
<td>IEI</td>
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PLANs UNDERWAY FOR RECYCLE WEEK 2008

UK recycling week 2008 will lift off 2/06/08 for a week of exciting, high profile activities focusing on the benefits of recycling. In 2007, TV presenter Denise Van Outen lent her name to the campaign, and similar celebrity support is expected for the 2008 event. The annual event, now in its 5th year, is organised by WRAP in partnership with leading materials recycling organisations: British Glass, Corus, Novelis, PaperChain and Recoup. Recycle week is also supported by national recycling campaigns in Scotland, Wales and N Ireland, together with a growing number of local authorities. Rebecca Cocking, recycling manager at British Glass said: “Recycling Week is an exciting opportunity every year to really promote the benefits of recycling, especially reaching out to people at the ‘grassroots’ level. With the crucial support we get from community groups and local authorities, it means we all have the chance to make a difference.” Plans for Recycle Week 2008 are well underway and regular announcements will be made outlining promotional activity and support materials available for local authorities and industry stakeholders and any other interested parties to plan their activities well in advance.


EU LAYS DOWN CLIMATE RULES

The UK has ‘welcomed’ the EC’s proposal for tackling climate change and delivering a low carbon economy in Europe. The package contains proposals to implement the decisions agreed by EU Heads of State and Government at the 2007 Spring European Council, including: a 20% reduction in EU greenhouse gas emissions by 2020; increasing to 30% when there is an international climate agreement; 20% of total EU energy consumption to come from renewables by 2020 and measures to support the development of carbon capture and storage including 12 demonstration projects. For the UK, the Commission’s proposals include; a cut of 16% in UK greenhouse gas emissions
from sectors not covered by the EU ETS by 2020; for 10% of road transport fuels to come from both renewable and sustainable sources. For more information see; www.defra.gov.uk/environment/index.htm


**COMMISSION ADOPTS AIR QUALITY DIRECTIVE**

A new European Directive that establishes new binding standards for fine-particle air pollution has been adopted this week by the European Commission. The move incorporates four existing Directives and one Council Decision into a single piece of legislation. The new Directive will require all Member States to reduce particulate matted exposure in urban areas by an average of 20 per cent between 2010 and 2020; exposure levels must be brought below 20 micrograms per cubic metre by 2015. However, the Directive does not alter existing EU standards for air quality, and allows Member States a considerable degree of flexibility with regard to the compliance time-scale.

“The European Union has today taken a decisive step in tackling a major cause of environmental and health problems,” commented Environment Commissioner Stavros Dimas. “European citizens are concerned about air pollution. “The new Directive on air quality addresses this concern by providing ambitious but realistic standards for fine particle PM 2.5 pollution in the European Union.”

*Source: EC Press Release April 2008*

**GREEN TAX BREAKS COULD SAVE UK £3BN, STUDY FINDS.**

UK businesses could save millions of pounds in National Insurance, tax and fuel costs by choosing low-emitting vehicles for their company-car fleets, according to the findings of research carried out by the Energy Saving Trust (EST). New regulations that entered into force on April 6th mean that cars that emit 120g or less of carbon per kilometre are eligible for a range of tax breaks. The EST notes that companies that take advantage of the regulations could make substantial savings in NI contributions and Benefit In Kind income tax.
payments as well as in fuel costs. If every business in the UK opted for low-emission company cars, the EST estimates, emissions for cars driven on company business alone would be cut by almost 2m tonnes per year. “The reasons are there for all to see: running vehicles costs a lot of money and with fuel prices over £1 a litre its not going to get cheaper any time soon,” commented EST head of transport Nigel Underdown. “I predict that 2008 will see a tipping point where offering and choosing low-emitting cars is the only sensible business option. “120 really is the magic number as far as people responsible for managing UK car fleets are concerned: implementing a green fleet policy could save a company with 50 cars up to £45,000 every year.”

Source: Retail Bulletin, April 2008
INTRODUCTION

Manufacturing industry is subject to a plethora of health and safety-related primary and secondary legislation either process or product-specific, whether national, European or international. Industry would not argue with the laudable objectives of such regulation but its ‘business case’ compels it to identify, understand, and then take steps to minimise the effects (i.e. costs) of any overlaps or interfaces there might be between regulatory regimes.

The inception of the REACH regulation, with the co-incidence of the Construction Products Directive and its Essential Requirement No. 3 (ER 3 - Hygiene, health and the environment) has presented the construction products’ sector with the need to examine both sets of provisions for potential interfaces in order to determine where they may be found, their nature, and any implications. A detailed analysis[1] was carried out ‘by industry’ ‘for industry’ in early 2008 under the auspices of the CEPMC, and what is presented here is a summary. The analysis establishes that sets of qualifying conditions can be


I.E.I. Secretary General - Dr. Silvano Pagliuca - on 19 Feb. 2008 attended a workshop on the possible interfaces between Construction Product Directive (CPD/ER3) and REACH.

Dr. Pagliuca believes the topic is very interesting for the world enamelling community and asked the permission of CEPMC to make the papers available for download from the I.E.I web site: http://www.iei-world.org/pagine/news/news02_2008.asp
derived that predict where potentially beneficial interfaces lie within REACH, where: an ER 3-related TC 351 test method (harmonised, horizontal); the ER3-related WT or WFT procedures; or the ‘intended uses’ identified in harmonised European Technical Specifications (ETS), could benefit manufacturers/importers with their obligations under REACH. Conversely, other sets of qualifying conditions describe where conflicting interfaces exist, so giving rise to potential confusion amongst manufacturers/importers between any limiting criteria, as Derived No Effect Levels (DNELs) and/or Predicted No Effect Concentrations (PNECs), derived under REACH and any limits (e.g. national pass/fail criteria) established for the same substance for use under CPD/ER 3. The REACH regulation has been taken as the ‘frame of reference’ because of the very strict deadlines associated with its obligations.

DISCUSSION

The REACH regulation came into force on 1 June 2007. REACH implements a uniform legal system, effective for all chemicals across the European Union/EEA. This system is intended to enhance the safe use of chemicals in all types of uses by placing obligations on a range of stakeholders. However, the REACH Regulation does not mention the term chemicals in its text but does address: substances, preparations and articles all of which are defined. And according to Article 1, REACH principally concerns the manufacture, import, placing on the market and use of substances on their own and in preparations and articles. It should be readily apparent, though, that most construction products are not substances. The majority are preparations and articles but even so, the obligations under REACH will, to a greater or lesser extent, affect manufacturers, importers, downstream users (formulators) and end-users of construction products. This will be the case even though preparations and articles, as such, are not the direct focus of REACH and even though construction products are already subject to the regulated dangerous substances initiatives under ER 3 of the CPD.

Evidently, manufacturers and importers of construction products that are actually substances will be most affected by REACH because it will achieve its primary aims by imposing a series of inter-related obligations for submission of a range of, essentially, self-assessed (but with some independent oversight)
information on the construction products that they manufacture (or import) into the EEA. Indeed the essence of REACH and CPD/ER 3 is ‘information’ and its ‘communication’ to relevant stakeholders [e.g. the European Chemicals Agency (ECHA), professional users, regulators and, ultimately, the general public] by way of a range of manufacturers’ declarations.

What then are ‘interfaces’? Interfaces (or overlaps) can be described as ‘points’ in the two legislative regimes where some informational aspect of REACH coincides with the same informational aspect of CPD/ER3. In particular, the ‘points’ at which these overlaps occur can be ‘defined’ by specific sets of qualifying conditions and can be described as either: a beneficial interface (useful overlap) or a conflicting interface (unwanted or confusing overlap). How can these sets of qualifying conditions be identified? This can only be done by analysing in detail each provision related to information and its communication in both the REACH regulation and CPD/ER 3 and then evaluating how one might impact upon the other.

For example, during registration under REACH, information on a substance is communicated to the ECHA in a Registration Dossier. Each Registration Dossier comprises, as a minimum, a Technical Dossier which records information on physicochemical parameters, toxicological effects and eco-toxicological effects of the substance. Could the derivation of this information give rise to an interface between REACH and CPD/ER 3? Possibly, but only if some aspect of the regulated dangerous substances initiatives under ER 3 addresses the determination of physicochemical parameters or toxicological or eco-toxicological effects of construction products that are, themselves, substances. With the exception of ‘ecotoxicity’, this will not be the case because CEN/TC 351 ‘Construction products – Assessment of release of dangerous substances’ is developing test methods in support of mandate M/366 but none of the methods will determine the physicochemical or toxicological characteristics of construction products. In the case of ‘ecotoxicity’, however, this is identified as a ‘sum parameter’ on the EC Indicative List of regulated dangerous substances and so TC 351 might develop an appropriate test method that could, potentially, be used by a manufacturer/importer in fulfilment of an obligation under REACH.
As a further example, a manufacturer or an importer of an ‘article’ must submit a registration under REACH if a substance is intended to be released from the article under normal or reasonably foreseeable conditions of use. Could this give rise to an interface between REACH and CPD/ER 3? Again, possibly, because CPD/ER 3 directly addresses the determination of release (or emission) of dangerous substances from construction products, many of which are articles. However, an interface - in this case the potential use of an appropriate CEN/TC 351 test method - will only occur under the following conditions; the substance is intended to be released as part of the design of the article; the substance is present in quantities greater than one tonne/year/registrant; the substance released (or emitted) is a regulated dangerous substance on the EC Indicative List; the article is a mandated construction product and the product is actually regulated for release/emission of the specific substance. These conditions form a set of qualifying conditions for a ‘beneficial interface’ e.g. the potential to use a method developed under CPD/ER 3 in support of an obligation under REACH.

As a final but important example related to registration, subject to a minimum tonnage, a Registration Dossier must also include a Chemical Safety Report (CSR). This is based either on a Chemical Safety Assessment (CSA) or, where a substance has also been classified as dangerous or is a PBT or vPvB, a Chemical Safety Assessment plus Exposure Assessment and Risk Characterisation. A detailed analysis shows that the latter type of CSA, but not the former, provides the main area where interfaces, whether beneficial or conflicting, will occur. The simpler form of CSA does not give rise to interfaces because it does not address release/emission of substances. However, the more comprehensive form of CSA includes exposure scenarios for a wide range of uses – effectively, from ‘cradle to grave’ – covering the substance (or any impurities in the substance) on its own, or in a preparation or in an article. Since variously, the substance or either a preparation or an article, in which the substance is used, could also be a construction product, there are potential interfaces with CPD/ER 3 because ER 3 concerns itself only with release/emission of dangerous substances from mandated construction products. A point to note is that, under REACH, the required information on release/emission may be obtained using any method available to the manufacturer (or importer) there is no obligation to use particular methods. Whereas, where interfaces occur, there then becomes the potential for a manufacturer (or
importer) to use an appropriate test method developed by CEN/TC 351, either during the ‘initial’ phases of registration, or later, were one to be validated and published in time for use.

A different obligation, ‘Notification’, applies where an article contains a substance of very high concern such as a CMR (category 1 or 2) or PBT or vPvB or endocrine disruptors, or substances of equivalent concern, above 0.1% by mass. If there are cases where a construction product, in the form of an article, contains a substance of very high concern, which is also a regulated dangerous substance on the Indicative List, then it is possible that a test method developed under CPD/ER 3 for determining the content of the relevant regulated dangerous substance could also be used for determining whether compliance with the 0.1% by mass limit has been met when notifying such a substance under REACH.

In the case of the WT (without testing) and the WFT (without further testing) risk-based ‘deemed to satisfy’ procedures under CPD/ER 3, the informational requirements vary. In the case of WT the requirement is for existing data to be submitted to validate release/emission of a set of product-specific regulated dangerous substances. In the case of WFT, any case submitted has to be based on results for release/emission obtained by using harmonised, horizontal test methods developed by TC 351. In either case, where there is an interface between REACH and CPD/ER 3 there exists the potential to use the results or official outcomes of either of these procedures in support of obligations under REACH, providing the results or official outcomes are actually ready in time for use.

With respect to the ‘intended uses’ of a product, each construction product-specific mandate identifies these for the purposes of the CPD. These intended uses are then reproduced within the relevant European Technical Specification (ETS) and could appear to give rise to an interface with REACH where ‘exposure scenarios’, ‘identified uses’ and ‘conditions of use’ of dangerous substances are concerned. However, the ‘intended uses’ in ETS are usually described in generalised terms whereas an analysis of REACH indicates that ‘identified uses’ within exposure scenarios need to be very precise and detailed in order to be able to derive DNELs (Derived No Effect Levels) and PNECS (Predicted No Effect Concentrations) for release/emission of substances. So, although there may be a theoretical interface between these two concepts from
the different legislative regimes, it seems unlikely that the descriptions of ‘intended uses’ in construction product ETS will prove to be very useful to manufacturers (or importers) with their obligations under REACH.

Where, however, DNELs and PNECs have to be derived for release/emission of a substance (or an impurity within a substance) as ‘limiting criteria’ in a CSA, there is the potential for a conflict to arise with any limits (e.g. national pass/fail criteria) established for the same substance (or impurity in the substance) for use under CPD/ER 3. The sets of qualifying conditions where this might occur have also been established in the full analysis reported by CEPMC and will not be repeated here.

Of the greatest significance in establishing whether or not there is any real benefit to manufacturers/importers of an interface, is the timeline for development of harmonised, horizontal test methods under CPD/ER 3 set against the ‘initial’ deadlines for obligations under REACH. If these timescales do not align, then any benefits will be limited. Construction products, which are either substances themselves or substances such as additives used in the manufacture of construction product/preparations/articles, will be manufactured (or imported) in the EEA in quantities greater than 100t/year. The initial registration deadline for such ‘phase-in substances’ is 31 May 2013 (commencing from 1 June 2008). Is it likely that either fully validated EN test methods for release/emission/content of regulated dangerous substances, or the WT/WFT procedures, will be published or ready in time for use before 31 May 2013? The main conclusions from the CEPMC’s detailed analysis are summarised below.
CONCLUSIONS

A large number of construction products will be affected by REACH [few of them by authorisation, some by registration (in particular substances)] but the great majority, as preparations or articles, will be subject to information flow obligations. There will be few interfaces, as these two regulations are more complementary than overlapping. Where interfaces do occur they should be mainly beneficial and consist of points in the two legislative regimes where: test methods developed by CEN/TC 351; the WT/WFT procedure developed for use with CPD/ER 3 and the intended uses identified for individual products in the corresponding European Technical Specification, could aid the manufacturer/importer in defining release/emission and conditions of use in exposure scenarios under REACH.

Conversely, there is the possibility of a conflict arising between limiting criteria, DNELs and PNECs, derived within exposure scenarios under REACH and any limits (e.g. national pass/fail criteria) established for the same substance under CPD/ER 3.

Last but not least, as this is the major conclusion, the strict deadlines in the REACH Regulation will compel manufacturers and importers to carry out necessary tasks and fulfil their obligations under REACH independently and before the harmonisation of ER 3 is completed. In particular the TC 351 test methods are very unlikely to be validated and published in time for use in registering any construction products/substances during the ‘initial’ phases of registration under REACH. Registration of substances manufactured (or imported) in the EEA in quantities of 100 tonnes, or more, per year, per registrant must take place before 31 May 2013 whereas the test methods under development by CEN/TC 351 are unlikely to be ready as ENs before the end of 2013. Were this prediction to be borne out for ‘initial’ registration, then the analysis of how to, and where to, find interfaces between REACH and CPD/ER 3 could still be of value. This would be where Registration Dossiers, for substances already registered, need to be updated with technical information derived from the use of test methods, as a consequence of using the substance in a new construction product or for a new identified use, and where it is possible to use the outcome of the WT procedure within REACH. The WT procedure will utilise existing/historical (empirical) data rather than test results obtained using a harmonised, horizontal test method developed by TC 351.
but, to be of use during the initial phases of REACH, the detailed administrative procedures and associated classification criteria would also have be in place within a very short, and perhaps unrealistic, timescale.
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ABSTRACT

The titanium dioxide opaque enamels were used as the basic enamel specimen. Using methyl-orange as the simulative pollutant solution for the photo-catalytic efficiency, we studied photo-catalytic activities of the titanium dioxide enamels. Crystal structure and microstructure of the TiO₂ were analyzed by means of scanning electron microscope (SEM) and X-ray diffract meter (XRD). Results showed that the photo-catalytic efficiency was greatly improved by the titanium dioxide enamel surface, and crystal of the TiO₂ was anatase at the firing temperature of 700°C. The enamels consisted of a lot of very small particles, those particles had very small size and very large surface dimension as well as very high chemical activity, which made the titanium dioxide enamels have excellent photo-catalytic degradation.
1. INTRODUCTION

Since photo-catalytic function of TiO₂ was discovered in 1972, the titanium dioxide has been widely used in the field of pollutant degradation, virus killer and environment protection. The titanium dioxide has the advantage of not only high photo-catalytic activity, but also good acid resistance, low cost and no poison, which makes the titanium dioxide become one of the best photo-catalytic agents [1-7].

A lot of research works on substrate materials for TiO₂ film, such as glasses, porcelains, fibres and metals, have been done [8-10]. So far, glasses coated with TiO₂ films have been manufactured and used for automobile windscreen with pollutant degradation and self-cleaning properties.

Steel sheet enamels have been widely used as decorating materials inside and outside buildings, subway stations and tunnels [11,12], and enamelling materials have also been used as bathtubs, boilers and vessels for food and water [13,14]. With the photo-catalytic property, these decorating materials and enamelling vessels could be self-cleaned and/or cleaned very easily as well as virus killer. But no report on the enamels of titanium dioxide opaque with the same properties has been published.

Since enamels are different from glasses and porcelains in chemical composition, structure and properties, specially, the soften point temperature and surface structure, it will influence the enamelling technology and TiO₂ structure as well as the photo-catalytic property [3, 12, 13].

In view of the potential pollutant degradation and self-cleaning properties of the titanium dioxide enamels, we made the special enamels with TiO₂ opaque, and studied their photo-catalytic properties. We also study the photo-catalytic mechanisms by investigating the microstructure and the crystal structure of the TiO₂ with the help of scanning electron microscope (SEM) and X-ray diffract meter (XRD).
2. EXPERIMENTAL DETAILS

2.1 Preparation of the titanium dioxide enamels

A TiO$_2$ opaque coating sheet was used as the basic specimen. Chemical composition of the coating is shown on table 1.

The coating frit is manufactured in accordance with the ordinary enamel frit manufacturing technology. The coating frit is mixed with suspension agent, electrolytes, and water. The mixture is milled into the slip and passed through 140-sieve mesh.

Then, the steel sheet (size: 50 x 50 x 1mm), which has been treated for removing oil and rust on the surface, is dipped into the coating slip for the enamel application. After the dipping, the enamelling specimen is dried and fired. The enamelling drying and firing temperature is 100 ± 5°C and 720 ± 10°C. The enamelling firing time is 240 seconds. The enamelling specimen has been made and the thickness of enamelling layer is 0.2 ± 0.05mm. The titanium dioxide enamelling samples were made.

2.2 Observation on photo-catalytic properties of the enamelling samples

Methyl-orange can be used as simulative pollutant solution to estimate photo-catalytic efficiency of the enamels according to references [15]. The concentration of the methyl-orange used in our work was 10mg/l. The coating samples were put into the glass vessels with diameter of 100mm, and 50ml methyl-orange solution was added into the glass vessels respectively. The enamelling samples were immerged in the solution for 1~13 hours. During the immerging, a 365nm low-pressure mercury ultraviolet (UV) lamp (20w UV light source) was positioned horizontally over twelve glass vessels with methyl-orange solution at about 80mm distances. Four of them were with the enamelling sample and four of them were without the coating sample. The temperature was 25 ± 1°C.

With the concentration of the methyl-orange solution changing, which was caused by the enamelling samples, its colour was changing at the same time. By observing the colour of methyl-orange solution with those coating specimens, the photo-catalytic efficiency of these enamelling samples would be determined.
After the artificial radiation with different time, the simulative pollutant methyl-orange solution was tested by a spectrophotometer HACH DR/2010 at 520nm.

### 2.3 The crystal structure and microstructure analysis

The titanium dioxide enamelling layers were removed from the enamels and ground into powder. The powder was analyzed with an X-ray diffract meter (Ragaku D/max 2550, Japan) (XRD) to investigate the crystal structure of the titanium dioxide enamel.

Microstructure of the titanium dioxide enamelling sample was analyzed by using a scanning electron microscope (EPMA-8705QH, Japan) (SEM).

### 3. RESULTS AND DISCUSSION

#### 3.1 Photo-catalytic activities

Relation between light absorption and concentration of methyl-orange at the 520nm [16] is as follows:

\[
A = 0.023 \times C + 0.011 \quad (1)
\]

Where \(A\) is light absorption

\(C\) is concentration of methyl orange (in mg/l).

In accordance with equation (1), we calculated the concentration changing of the methyl-orange solution before and after the radiation of 365nm.

The degradation rate of methyl-orange, which represents the photo-catalytic efficiency of the coating, can be determined by equation (2):

\[
d = \frac{(C_0 - C)}{C_0} \times 100\% \quad (2)
\]

Where \(d\) is degradation rate,

\(C\) is concentration after radiation,

\(C_0\) is concentration before radiation.
Fig. 1 shows the relation between the radiation time of the methyl-orange under UV lamp and the degradation rate of the methyl-orange with and without the enamelling specimens. The values on the fig. 1 are the average of four specimens. It shows that the degradation rate of methyl-orange solution under the same radiation condition is different. Among the methyl-orange solutions, the one with the titanium dioxide enamel changed much faster than the other one.

After radiation of 11 hours, the degradation rate of the methyl-orange with the titanium dioxide enamelling sample was over 80%, while that of the methyl-orange without enamelling sample were 20%. It indicated that the TiO$_2$ opaque enamelling accelerated degradation of the methyl-orange solution because there was some TiO$_2$ in the coating (see fig. 2).

Table 2 shows the relation between the firing temperature of the titanium dioxide enamels and degradation rate of methyl-orange under radiation of 13 hours. It showed that the degradation rate of methyl-orange increased with the firing temperature enhancing when the firing temperature was lower than 650°C, and degradation rate of methyl-orange decreased with the firing temperature enhancing when the firing temperature was higher than 750°C. Therefore, the optimum firing temperature range of the TiO$_2$ enamels with the best photo-catalytic efficiency was between 650°C ~ 750°C.

### 3.2 Crystal structure and microstructure of the TiO$_2$ coatings

Fig. 2 shows the crystal structure of the TiO$_2$ enamel under different firing temperatures. It indicated that most crystals of the TiO$_2$ enamel were anatases when the firing temperature was below 700°C. With the firing temperature increasing, the crystal peak strength increased and the crystal peak width became shorter, which indicated that the crystal structure became perfect. Considering table 2, we concluded that with the firing temperature increasing, anatase with perfect crystal structure had promoted degradation of the methyl-orange solution.
Fig. 3 shows the microstructure of the TiO$_2$ enamel with 720$^\circ$C firing temperature. Small crystals in the enamel surface was discovered, which were tested to be anatases according to Fig. 2, and the size of those crystals was among 0.1~0.3µm. Fig. 3 also shows that the surface of the TiO$_2$ enamel surface is dense and smooth without bores.

Fig. 4 shows the super-microstructure of the TiO$_2$ enamel with 720$^\circ$C firing temperature, which has been enlarged for 20,000 times. It can be discovered from fig. 4 that the TiO$_2$ enamel surface with 720$^\circ$C firing temperature consists of a lot of very small particles. Since those small particles have very small size (0.01~ 0.05µm and/or 10~50 nano), it must have very large surface dimension, and very high chemical activity, which makes the TiO$_2$ enamel surfaces have excellent photo-catalytic degradation (see fig. 1).

3.3 Photo-catalytic performance of the titanium dioxide enamels

Reports on TiO$_2$ as catalyst for removing organic compound pollutant in water by using UV and/or sunlight have been published$^{[1-3, 15, 16]}$. The Photo-catalytic degradation reaction of methyl-orange occurred on the surface of TiO$_2$, whose forbidden gap energy of 3.2ev was approximately equal to the photon energy of 387.5nm UV light. When the TiO$_2$ was exposed to irradiation of 365nm UV light, electron hole with high chemical activity would be produced$^{[17]}$:

$$\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2 + e^- + h^+ \quad (3)$$

When those electron holes moved to the surface of the TiO$_2$, they brought on a series of oxidation-reduction reaction, which were as follows:

$$\text{H}_2\text{O} + h^+ \rightarrow \cdot\text{OH} + \text{H}^+ \quad (4)$$
$$\text{O}_2 + e^- + \text{H}^+ \rightarrow \text{HO}_2^- \quad (5)$$
$$\text{HO}_2^- + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O}_2 \quad (6)$$
$$\text{H}_2\text{O}_2 + e^- \rightarrow \cdot\text{OH} + \text{OH}^- \quad (7)$$

The oxidizing power of $\cdot\text{OH}$ was strong enough to decompose almost all the organic materials into $\text{H}_2\text{O}$ and $\text{CO}_2$: 
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\[
\begin{align*}
RCH_2-CH_3 + 2OH^- \rightarrow & \quad RCH_2-CH_2-OH + H_2O \\ 
R-CH_2-CH_2-OH + \cdot OH \rightarrow & \quad RCH_2CHO + H_2 \\ 
RCH_2CHO + \cdot OH \rightarrow & \quad RCH_2COOH + H_2 \\ 
RCH_2COOH + \cdot OH \rightarrow & \quad RCH_3 + CO_2
\end{align*}
\]  

When the intensity of light is constant, the number of \( \cdot OH \) will increase with the radiation time increasing. Therefore, as long as the radiation time is long enough, the organic materials, such as, methyl-orange can be completely photo-degraded into H\(_2\)O, CO\(_2\) and mineral acids \(^{[15, 16]}\).

Since there was over 25\% TiO\(_2\) in the TiO\(_2\) opaque enamel, it should be reasonably concluded that the coating with TiO\(_2\) opaque had the photo-catalytic property of removing organic compound pollutants in water under UV radiation (see fig. 1). The fact, that TiO\(_2\) opaque enamels have photo-catalytic property, indicate that TiO\(_2\) opaque enamels can be used as bathtubs, water tanks and food vessels as well as decorating materials outside building, in which natural ultraviolet and/or sunlight can radiated, for pollutant degradation and self-cleaning as well as virus killer.

Besides, the titanium dioxide enamel surface with anatases opaque have very small size (see fig. 4) and very large surface dimension as well as very high chemical activity, which make the titanium dioxide enamel to have the excellent photo-catalytic degradation (see fig. 1).

4. CONCLUSIONS

The enamels with opaque of titanium dioxide have the properties of the photo-catalytic, the pollutant degradation and self-cleaning under ultraviolet light irradiation.

The titanium dioxide coating at the firing temperature of 720°C consists of a lot of very small particles (0.01 ~ 0.05\( \mu \)m and/or 10 ~ 50 nano). Those particles have very small size and very large surface dimension as well as very high chemical activity, which make the coating with TiO2 opaque have excellent photo-catalytic degradation.
Table 1: Chemical composition of the TiO$_2$ opaque enamel

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>B$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>Na$_2$SiO$_4$</th>
<th>P$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percent</td>
<td>25 - 35</td>
<td>1.0 - 5.0</td>
<td>8.0 - 12</td>
<td>25.0 - 35.0</td>
<td>1.0 - 5.0</td>
<td>10.0 - 15.0</td>
<td>3.0 - 6.0</td>
<td>1.0 - 3.0</td>
</tr>
</tbody>
</table>

Table 2: Relation between the degradation of methyl-orange and the firing temperature of the titanium dioxide enamels

<table>
<thead>
<tr>
<th>Baking temperature /°C</th>
<th>600</th>
<th>650</th>
<th>700</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degradation /%</td>
<td>89.6</td>
<td>94.5</td>
<td>95.2</td>
<td>92.0</td>
</tr>
</tbody>
</table>

Fig. 1: Relation between radiation time and degradation rate of methyl-orange
Fig. 2: Crystal structure of the titanium dioxide enamels with different firing temperature.

![Crystal structure diagram with peak intensities at different temperatures.](image)

Fig. 3: Microstructure of the titanium dioxide coating surface (x 5,000)

![Microstructure image with labels and scale bar.](image)
Fig. 4: Super-microstructure of the titanium dioxide coating surface (x 20,000)

REFERENCES
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THE EFFECT OF REFRACTORY MILL ADDITIONS ON THE THERMAL EXPANSION OF ENAMEL

INTRODUCTION

Crazing, spalling, warp and other problems are caused by stress that develops between enamel and the steel substrate during the cooling cycle of the firing process. This effect is due to the differences in the coefficients of thermal expansion (CTEs) of the two materials. Above the glass transition temperature \( T_g \), in the process of cooling, the stress is relieved first by the viscous flow and, at the lower temperatures, by the plastic deformation of the enamel.

The stress begins to build up when the glass viscosity increases to such a level that the deformation of the enamel changes from plastic to elastic. The temperature of this transition is close to the \( T_g \cdot T_g \) and can be measured from the glass expansion curve (Figure 1).

The incipient fusion point (IFP), \( T_g \), and CTE are functions of the glass composition and, therefore, are related. If we consider these factors independent and everything else equal, the difference in stress of an enamel at room temperature (20°C) that has a \( T_g \) of 500°C (typical) and an enamel with a \( T_g \) 25°C lower is \((500 - 20)/(475-20) \approx 105\%\). In other words, a 25°C increase in \( T_g \) increases compressive stress as much as it decreases CTE from \(315 \times 10^{-7}\, ^\circ\text{C}^{-1}\) to \(300 \times 10^{-7}\, ^\circ\text{C}^{-1}\). From practical experience, this is a very substantial difference that should be considered (Figure 2).
Figure 1: Thermal expansion curve of glass.

Figure 2: Inherent stress in enamels A and B in relation to thermal expansion of enamel and iron.\textsuperscript{[6]}
Actually, the difference in stress ($\sigma$) is even more substantial, because the glass with a lower $T_g$ is usually softer. Softer glasses usually have lower moduli of elasticity (E). Because $\sigma$ is directly proportional to E, a decrease in E decreases the stress. Also, an increase in $T_g$ decreases maximum tensile stress at $\sigma_m$, which also contributes to the increase in compressive stress.

The cause of hairline is tensile stress. In addition to the stress that develops at the cooling of the system from $\sigma_o$ (IFP) to $\sigma_m$ ($T_g$), where the enamel CTE is higher than the steel substrate CTE. IFP is the point where enamel begins to exhibit plastic deformation. The higher the $T_g$, the lower is the maximum inherent stress at $\sigma_m$. Lower stress at $\sigma_m$ corresponds with higher $\sigma_o$ temperature and the wider range where the glass is safely under compressive stress (Figure 2). Therefore, to improve crazing resistance, $T_g$ should be increased. Practically, this is achieved by making the glass harder. Even in this simplified model, the CTE of the glass cannot describe stress development in the enamel. The initial tensile stress above the $T_g$ point is a function of CTE and $T_g$ and IFP. These parameters are not directly related to the low-temperature CTE.

It is impractical to address each stress-related problem by developing a new frit. Stress can be controlled by the addition of refractory materials in the mill formula. Some of these additions dissolve in glass slowly and mostly stay in the enamel as a separate phase. We refer to these additions as refractory to distinguish them from other high temperature oxides, such as calcium and magnesium oxides that easily dissolve in glass.

Many factors other than CTE, IFP and $T_g$ influence stress in an enamel-steel system. The properties of the steel – E, CTE and thickness and shape of the substrate and among them.[7]

The structure and the composition of the enamel are also very important. Defects such as micro-cracks and bubbles relieve stress. The iron oxide penetration layer on the enamel-substrate interface creates a transitional layer, which is different from the volume of enamel. The relief of stress through the plastic deformation of enamel is a time-related process; therefore, the speed of cooling also is a factor in stress development. These, along with many other factors, are beyond the scope of this study.
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The purpose of this work is to study the effect of mill-added refractory on Tg and of the enamel.

Table 1. Tg of Ground Coat Enamel with 20% Refractory, Fired at Different Temperatures

<table>
<thead>
<tr>
<th>T (°F)</th>
<th>As is</th>
<th>Feldspar</th>
<th>ZrO₂</th>
<th>TiO₂</th>
<th>ZrSiO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>298</td>
<td>292</td>
<td>269</td>
<td>276</td>
<td>257</td>
</tr>
<tr>
<td>1500</td>
<td>298</td>
<td>286</td>
<td>274</td>
<td>287</td>
<td>253</td>
</tr>
<tr>
<td>1600</td>
<td>299</td>
<td>289</td>
<td>270</td>
<td>284</td>
<td>249</td>
</tr>
</tbody>
</table>

PROCEDURE

The most common refractory materials used as mill additions are silica (SiO₂), titania (TiO₂), zircon (ZrSiO₄), zirconia (ZrO₂), and feldspar. All these materials are present as a separate phase in fired enamel. The mineral composition of feldspar is 57% albite, 6.1% anorthite, 24% orthoclase, 10.2% silica and the balance mica. Density and CTE of this composition were calculated based on individual data from references [1] - [3].

In ceramic practice, volume CTE is used to avoid the problem of anisotropic thermal expansion. Consequently, where not stated otherwise, mill additions are expressed in volume percent, as a percentage of the frit.

The mill formula is 100g frit, variable refractory, 3g ball clay, 0.3g bentonite, 0.2g NaAlO₂, 0.2g K₂CO₃, and 45g H₂O.

The clayless, bubble-free formula is 100g frit, variable refractory, 0.02g Peptapon 99 and 45g H₂O.

The composition was milled to a fineness of ~6%/200 mesh.

The material was dried and fused into bars about 4mm x 4mm x 50mm in nickel containers at 1500°F (if not stated otherwise) for 12 min. At the cooling cycle, the bars were annealed with soak temperatures of 482°C for 60 min, 454°C for 30 min, and 399°C for 30 min, with a ramp speed of 2°C/min.
RESULTS AND DISCUSSION

In all studied ranges of materials and concentrations, there is little variation in the value of \( T_g \). Everywhere, \( T_g \) is \( \sim 500°C \pm 10°C \). There is some trend for \( TiO_2 \) to increase in \( T_g \) from 496°C to 505°C - 510°C. Feldspar tends to decrease in \( T_g \) to 485°C - 490°C. No connection between \( T_g \) and porosity or amount of refractory is detected. Consider that the thermal expansion curve is not perfectly linear; the difference in \( T_g \) is within normal variation. If the process of refractory dissolution in the glass would be significant, it would be reasonable to expect a significant change in \( T_g \).

Only the general observation that addition of refractory somehow decreases CTE could be made on compositions with developed bubble structure (clay-containing system). The variability of the measured CTE is so great that no meaningful relation between refractory content and CTE of the enamel could be found. Decrease in clay content does not decrease variability, however. Only bubble free samples yield meaningful results. If one were to regard bubbles as inclusions in enamel, then size and concentration of bubbles should influence the CTE. Consider that bubble structure in the relatively thick specimens is hard to control; high variability of results should be expected.

The study was done on semi-opaque and ground coat frits. The former was selected as a frit where various refractory materials are often added and the latter as a generic ground coat frit where stress control is important.

No meaningful results were obtained on semi-opaque frit. It was found that refractory particles promote crystallisation of \( TiO_2 \) from the semi-opaque glass at an unpredictable rate. Additional \( TiO_2 \) crystals contribute to thermal expansion, which causes results to vary.

There is no significant difference in CTE between materials fused at 1400°F, 1500°F, and 1600°F (Table 1). Possible explanations could be that no or little dissolution of refractory in glass takes place in the studied temperature range or that the difference in CTE between heterogeneous system refractory-glass and the homogeneous glass of the same composition is small.

After many trials, it was established that variation of CTE in \( SiO_2 \)-containing enamel was much higher than in other compositions. For all systems with the exception of \( SiO_2 \), CTE variation was \( \pm 1.5% - 2% \). For \( SiO_2 \) the variation was
±4% - 5%. Even the well-known fact that mill added SiO₂ increases hairline resistance and promotes crazing cannot be correlated with the thermal expansion data. X-ray diffractometry of the slowly annealed specimen and the water quenched specimen shows that only α-quartz exists in all temperature ranges. There is no SiO₂ phase transition that would make the results vary. Probably unlike other refractories, SiO₂ reacts or/and dissolves in glass with an unpredictable rate. This process significantly influences CTE.

The CTE-refractory-content relation for other refractories is close to linear (Figure 3).
The relative effect of refractory on CTE does not correspond with CTE of the individual refractory materials (Table II), as expected. The CTE of the phases is just one of the factors in the CTE of the composite. The other factors that pertain are modulus of elasticity and Poisson’s ratio. The CTE of the composite material is given by

\[ \alpha = \sum \alpha_i K_i V_i / \sum K_i V_i, \]

Where \( K = E/(3(1-2\mu)) \), \( E \) the elastic modulus, \( \mu \) the Poisson ratio, \( \alpha \) the volume expansion coefficient, and \( V \) the volume part of the phase. Nevertheless, this data can be useful in the estimation of the composite enamel CTE.

Also, the CTE of the crystalline materials is a nonlinear function of temperature. For example, for MgO from 50°C to 500°C, CTE changes from \(~200 \times 10^{-7}\)°C\(^{-1}\) to \(~390 \times 10^{-7}\)°C\(^{-1}\). \[1\]

<table>
<thead>
<tr>
<th>Refractory</th>
<th>Literature</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrSiO(_4)</td>
<td>104</td>
<td>126</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>181</td>
<td>300</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>229</td>
<td>240</td>
</tr>
<tr>
<td>Feldspar</td>
<td>239</td>
<td>161</td>
</tr>
</tbody>
</table>

The CTE of the ground coat that was calculated from the linear regression equations (Table II) is the same as the directly measured one. That again, raises the question if there is dissolution of refractory in glass or if this dissolution does not affect the CTE.
We apply three different models to calculate change in the CTE with 10% vol. of refractory in enamel (Table III). The first model uses Winkel-Mann Schott (W&S) factors supplemented by Mayer et al.\textsuperscript{[5]} The second model is based on Appen mol. Factors.\textsuperscript{[4]} Both calculations assume the total dissolution of refractory in glass. The third calculation is an average of the individual CTE proportionally to the volume content of the phases.

Table III shows that all three calculations give results similar to the experimental ones. That means CTE data are not reliable evidence for or against the dissolution of refractory in glass.

Feldspar decreases the CTE of enamel to a lesser extent than other refractories. A possible explanation is the presence of alkali metals in feldspar, which increases glass CTE far more than do other oxides.

Feldspar should be recommended when enamel is to be hardened without an increase in the compressive stress, as in case of spalling problems.

Table III. Changes in CTE with 10 vol.% of Refractory in Glass

<table>
<thead>
<tr>
<th></th>
<th>TiO₂</th>
<th>ZrO₂</th>
<th>ZrSiO₄</th>
<th>Feldspar</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTE</td>
<td>240</td>
<td>300</td>
<td>126</td>
<td>161</td>
<td>15</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>4.26</td>
<td>5.89</td>
<td>4.56</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>W&amp;S</td>
<td>-17</td>
<td>-6</td>
<td>-10</td>
<td>-1</td>
<td>-19</td>
</tr>
<tr>
<td>Appen</td>
<td>-3</td>
<td>0</td>
<td>-11</td>
<td>-12</td>
<td>-29</td>
</tr>
<tr>
<td>Average CTE</td>
<td>-4</td>
<td>-5</td>
<td>-11</td>
<td>-5</td>
<td></td>
</tr>
</tbody>
</table>

CONCLUSIONS

- Refractory additions, while they make enamel harder, do not change T₉. The traditional explanation why harder enamel is more resistant to hairlines is not applicable to heterogeneous enamels.

- The thermal expansion data have been successfully used for years to predict frit performance. There is good correlation between frit CTE and resistance to crazing, hairline and spalling of enamel. As for multiphase enamel, the correlation is more complicated, and other factors should be taken into account.
• The CTE of individual phases of enamel alone are not a reliable factor to predict enamel thermal expansion and the stress in enamel. Glass interaction with refractory, bubble structure and other factors substantially influence the enamel CTE.

• Stress related enamel behaviour correlates with various enamel properties. All these properties are related to enamel composition. In some cases, enamel behaviour could be better explained by other than CTE properties. In these cases, correlation of this behaviour with CTE just reflects common relation to the enamel composition.

• There is no polymorphic inversion in mill-added quartz during the firing cycle.

• Of the studied additions, feldspar is the least and zircon is the most efficient in decreasing enamel thermal expansion.

• Thermal expansion of enamel linearly correlates with the amount of refractory material added.

REFERENCES


OBITUARY – Peter Duff

It is with deep sadness that we report the death of Peter Duff the day before his 76th birthday on the 27 February 2008 after a prolonged time in hospital and nursing home. He had completed over 43 years service with Stewart and Gray Ltd and Escol Products Ltd., joining the company in 1951 and retiring in February 1995.

After a short time working in the carpet business Peter started with the company working on box furnaces handling heavy castings, this was excellent shop floor training, but Peter was anxious to improve his knowledge of the vitreous enamel process and when a vacancy arose in the laboratory he applied and was successful, he then applied for the position of sales and service representative and was again successful. He found it difficult at first to understand how other representatives could drive from the south to the north of the U.K. without using a map, however after many factory visits he was soon doing the same.

He soon established himself as a knowledgeable practical enameller with the ability to solve problems especially the enamelling of cast iron, this was much appreciated by customers worldwide. He not only built up a strong relationship with customers but in many cases with their families as well. He was also at ease in having meetings at all levels when visiting companies. His calm and friendly approach was a great asset and built up life long relationships.

Although work took up much of Peter’s time he did have interests away from enamelling. He was very keen on sea fishing and his sea rod nearly always accompanied him together with cans of enamel on his many visits to Ireland. He also supported local boxing clubs and became involved in the welfare of boxers.

We send our condolences to Pat and his two daughters Sally and Julie and their families.

Jim Gray
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