The Vitreous Enameller

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First of all, I would like to extend my thanks for Dr. Simon Cook for his 2 year service as Chairman.

His Chairmanship coincided with probably the worst economic crisis we have experienced since the 1930’s, but under his guidance, and with the help of Council we seem to have weathered the storm. We are also making progress in securing the long term future of the IVE.

As you are aware we are currently pursuing a merger with IOM_, and it’s quite interesting to note that after the General Election the Conservative and Liberal Democrats seem to be following our lead.

As you may know I have been retired for just over 12 months now, and as I’m sure you’ve heard said many times. “I don’t know how I found time to go to work.”

I am however fortunate, as after two successful hip operations I am now more mobile and pain free. For this I am indebted to the NHS. The downside is airport security where I set off the alarms, but this is a small inconvenience when compared to the benefits.

On a more serious note.

Sadly, I have to report that in April I received a card from Johanna, the wife of Bob Maertens, informing me of his death. He had been suffering from cancer for quite a few years. Bob was well known throughout the world and a very well respected technician.

In the last few months it has also been very sad to see the demise of Escol Products, and also more recently, from a personal point of view the closure of Bilston and Battersea Enamels.

Bilston and Battersea Enamels started as an offshoot of English Vitreous Enamels (Bilston) Ltd., where I worked in the frit laboratory after leaving school in 1962. Copper Enamels (Bilston) Ltd., was formed in 1968 and later became Bilston and Battersea Enamels Ltd., I can remember our old chief chemist, Bill Porter cutting up copper pipe to make serviette rings and
enameling them in strong cobalt blue. And so began the renaissance of enameling on copper. The company went from strength to strength, and supplied Halcyon Days in London from 1969 until 2008. Fortunately, on a brighter note, Halcyon Days Studios are still producing and exporting their intricate enameled copper boxes.

But looking to the future.

I am confident; the IVE in the capable hands of Chairman Mark Nutting, and with the help and support of Council will take the IVE forward, and the most beneficial way I believe is the merger with IOM_.

So finally, many thanks to Council and the working group, under the leadership of Dr. Simon Cook, (our S.W.O.T. expert), for all their dedication and hard work.

Ben Fieldhouse
IVE Honorary Treasurer

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EAST MIDLANDS MATERIALS SOCIETY

A Local Society Affiliated to the Institute of Materials, Minerals and Mining
In conjunction with the Surface Engineering and Light Metals Divisions of the Institute of Materials, Minerals and Mining has organised a regional conference on:

“Future Directions for Surface Engineering”
On Tuesday 29th June 2010.

SPONSORSHIP

Sponsorship is flexible, but suggested packages are:

£150 will allow one small display, one attendee at the conference and a mention as a sponsor, with corporate logo. Extra personnel will be allowed to attend, subject to an extra payment of the conference fee or refreshments at cost.

£250 will allow a display, two attendees at the conference and mention as a sponsor, with corporate logo. Extra attendees will be allowed, conditions as above.

Further details and expressions of interest: Please contact the organisers;
Gary Critchlow (g.w.critchlow@lboro.ac.uk, phone 01509 222949),
Dave Evetts (dave_evetts@hotmail.com, phone 07905 322107)
or Keith Harrison (k.harrison428@btinternet.com, phone 07786 585030).

Venue: Riverside Conference Centre, Derby DE24. 8HY. For directions and other venue information see www.theriversidecentre.co.uk.
EVENTS CALENDAR

29 June 2010  
Future Technologies, Applications and Opportunities for Surface Engineering  
Venue: Derby, UK  
Contact: Dave Evetts  
Tel: 01159 733525 or 07905 322107  
Email: dave_evetts@hotmail.com  
Web: http://www.iom3.org/emms

18 July 2010 - 20 July 2010  
1st UK-China Steel Research Forum  
Venue: Leicester Conference Centre, Leicester, UK  
Contact: Dr Hongbiao Dong  
Tel: +44 (0)116 2522528  
Email: h.dong@le.ac.uk  
Web: http://www.uk-china-steel.net/

19 July 2010 - 21 July 2010  
Latin American Iron & Steel Trends  
Venue: Rio de Janeiro, BRAZIL  
Contact: Tania Biggs  
Tel: +44 (0) 20 7903 2263  
Email: sandra.napientek@crugroup.com  
Web: http://crugroup.com/events/cruevents/pages/default.aspx

25 August 2010 - 29 August 2010  
5th Mid-European Clay Conference (MECC2010)  
Venue: Budapest, HUNGARY  
Contact: Klára Lang  
Tel: (+36 1) 457 0542, (+36 20) 9252 816  
Email: diamond@diamond-congress.hu  
Web: http://www.diamond-congress.hu/
08 September 2010 - 10 September 2010
Society of Glass Technology
Annual Conference
Venue: Cambridge, UK
Contact: Christine Brown
Tel: +44 (0) 114 263 4455
Email: christine@glass.demon.co.uk
Web: http://www.sgt.org/cgi-bin/open.cgi?page=index

14 September 2010 - 16 September 2010
First Centre for Advanced Structural Ceramics
Summer School on Ceramics
Venue: Imperial College London, UK
Contact: Fraser Wigley / Eduardo Saiz
Email: f.wigley@imperial.ac.uk
       e.saiz@imperial.ac.uk
Web: http://www3.imperial.ac.uk/structuralceramics/

27 September 2010 - 01 October 2010
Tecnargilla 2010 - the Future of Ceramics
Venue: Rimini, ITALY
Contact: Event Organiser
Tel: 059.510.336
Email: info@acimac.it
Web: http://www.tecnargilla.it/

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UK MANUFACTURING CONTINUES RAPID EXPANSION

UK manufacturing expansion is being sustained at its fastest rate for almost 16 years but factories must diversify to avoid being hit by government cutback warned an expert as new upbeat figures were released today (1 June) by the well respected Chartered Institute of Purchasing and Supply (CIPS).

The Institute’s Manufacturing Purchasing Managers’ Index (PMI) – which is calculated from data on new orders, production, employment, supplier performance and stocks of purchases – steadied at 58.0 and has now remained above the no-change mark of 50.0 for eight consecutive months. May saw manufacturing production rise for the 12th successive month and the rate of expansion stay close to March’s fifteen-and-a-half year high.

Commenting on the report, Graeme Allinson, head of manufacturing, transport and logistics at Barclays Corporate, said: “British producers have certainly been quick to take advantage of any glimmer of increased confidence, adjusting their business operations to mirror levels of demand and looking to target international markets. It is essential for manufacturers to ensure they are not over-dependent on the government purse over the coming years however, as public spending around the world is increasingly squeezed by deficit reduction. In the UK there has been clear indication that spending cuts will be widespread and with 55 per cent of UK manufacturing supplying the home market, diversification, both in terms of import vs export and also the private vs public sector client mix, should be the order of the day.”

Growth of output was supported by a further robust increase in new orders. Improving market conditions and successful promotional efforts underpinned an 11th successive month-on-month increase in total new orders. Growth in new work was only slightly below April’s six-year peak. Meanwhile, increased demand from China, Europe, the US, the Middle East and Africa led to a further near survey-record increase in new export orders. A number of firms indicated that the relatively weak sterling exchange rate continued to aid sales efforts in overseas markets.
The latest survey suggested that the inventory cycle remains supportive of future production growth. There was also anecdotal evidence from manufacturers that part of the gain in new orders reflected clients rebuilding their stock holdings.

Employment rose for the second month running in May with increased employment being linked to rising production requirements and an accumulation of work-in-hand at manufacturers.

Average purchasing costs increased at the fastest rate since August 2008 with companies reporting higher prices for chemicals, fuels, metals, packaging, paper and timber. The weak sterling exchange rate also raised the cost of some imported inputs.

CIPS CEO David Noble said the strength of recovery of the UK manufacturing sector had taken everyone by surprise – “this time last year, the industry was on its knees”. He went on: “While the turnaround so far this year is obviously good news, we can’t forget this has been driven in large part by the weak sterling exchange rate bolstering export demand. Problems in countries such as Greece and Spain have strengthened the pound against the Euro recently and could also have a severe impact on the Eurozone economy. Given the euro countries are Britain’s biggest trading partners, any double-dip recession there would undoubtedly damage the UK manufacturing sector.

“There are also additional troubles looming on the horizon which could constrain the pace of recovery. The boost from the inventory cycle will eventually wane, as firms stop balancing their stock, meanwhile, the new government’s austerity measures will undoubtedly dampen the domestic market. Despite all this, the increase in manufacturing jobs is very good news, not just for the health of the sector but for the UK economy as a whole. Higher employment means more money in the pockets of consumers which will have a positive knock-on effect on other parts of the economy and finally get us on the homerun.”
The CIPS report’s author, Rob Dobson, senior economist at Markit said UK manufacturing had maintained its “blistering” start to the second quarter although production remained well below pre-recession levels. “This rapid growth is stretching capacity, leading to a survey-record increase in backlogs of uncompleted orders,” he went on. “The good news is that this encouraged employers to boost staffing levels again, and a strong rise in orders for plant and machinery suggest that companies are also boosting their investment spending.”

However, Dobson warned that, “growth was driven by a combination of robust demand from domestic customers and a strong export performance, both of these sources of new orders may disappoint as we move into the summer.”

Source: Works Management Website (www.worksmanagement.co.uk) – 1 June 2010
EXPORTS DRIVE UK MANUFACTURING IMPROVEMENT

Foreign demand for UK manufactured goods has strengthened further, with export order books above par for the first time in over two years, although overall demand is still lagging, the CBI said yesterday (17 May).

Responding to the latest CBI monthly Industrial Trends Survey, 27% of manufacturers said that export orders were above normal, while 24% said they were below. The resulting balance of +3% shows that export orders are no longer sub-par, having improved considerably on April. This month’s result is the first positive survey balance since March 2008.

In comparison, total order books are not quite so healthy, reflecting the slower recovery in domestic demand. However, the balance of 18% of firms reporting orders to be below normal was also a significant improvement on April and orders are now back in line with the long-run average.

With demand improving, manufacturers expect to raise output firmly during the next three months, with a net 17% expecting production to rise, which is slightly stronger than April.

However, the CBI said inflationary pressures remained significant and domestic prices are expected to rise over the next three months, with a balance of 14% of firms expecting prices to head upwards, similar to levels of the past two months.

CBI chief economic adviser Ian McCafferty said the weak pound had made UK exports more attractive, and manufacturers were benefiting from the pick-up in world trade. “This is helping the recovery in manufacturing, and a slightly stronger rise in production is predicted in the coming months. Firms also expect to raise prices again over the coming three months because of higher energy costs and import prices.”

Source: Works Management Website (www.worksmanagement.co.uk) – 18 May 2010

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BUSINESSES URGED TO MAKE WEEE EFFORT

Anyone importing, rebranding or manufacturing electrical or electronic equipment must register with the Environment Agency under the Waste Electrical and Electronic Equipment (WEEE) Regulations. Breaching the regulations can lead to a court appearance and the threat of a large fine, of up to £5,000 in the Magistrates’ Court, or without limit in the Crown Court.

The regulations were brought in to reduce the amount of waste electrical and electronic equipment being produced and to encourage businesses to reuse, recycle and recover more.

Every year, the UK throws away around two million tonnes of waste electrical and electronic equipment, which is one of the fastest-growing types of waste in the UK and the EU.

The EU adopted the WEEE regulations to deal with this waste and make sure more is collected for treatment and recovery and less goes to landfill. Manufacturers and importers of electrical equipment now are obliged to offer to take back redundant equipment.

Relevant equipment includes computers, televisions, photocopiers, power tools, lighting, large and small household appliances, and toys. The regulations, which came into force in early 2007, also apply to businesses which sell or are disposing of electrical or electronic equipment, and aim to prevent illegal exports.

The Environment Agency is working with regulators in the UK and overseas to catch rogue operators illegally exporting waste electrical and electronic equipment abroad, where items often are dismantled in unsafe conditions and the remains dumped, both of which pollute the environment and pose a risk to human health.
“We are happy to give advice to businesses about their obligations and I would urge anyone needing guidance to call us or visit our website,” said WEEE team leader Peter Stevenson. “We’re always looking, in a variety of ways, to identify companies which potentially should be registered.

“We will contact businesses to check and, if we discover they should have been registered, it is our policy to prosecute. If we prosecute, we will bring charges for every year that the business was not registered.”

On registering, businesses pay a registration fee and confirm how much electrical and electronic equipment they deal with each year.

A compliant business has a responsibility to meet the cost of treating and recovering waste electrical and electronic equipment and there are different collection and funding arrangements for domestic and non-domestic equipment.

When disposing of any waste, including waste electrical and electronic equipment, all businesses must ensure that their waste goes to a registered waste operator which will deal with it correctly and within the law.

More information about WEEE and businesses’ responsibilities under the regulations can be found at the Environment Agency website at www.environment-agency.gov.uk/weee.

Source: Environment Agency Website (www.environment-agency.gov.uk) – 23 March 2010
NEW CARBON TRADING SCHEME TO RANK BIG UK BRANDS ON ENERGY EFFICIENCY

New rules that come into force today will pitch some of the UK’s largest organisations against each other in a drive to cut carbon dioxide (CO₂) emissions.

For the first time large non-energy intensive organisations, which account for about 10% of UK CO₂ emissions, will be legally bound to closely monitor and report their emissions from energy use in preparation for carbon trading. The scheme will also give people and businesses the opportunity to compare organisations’ efforts to combat climate change for the first time.

The Government scheme, known as the CRC Energy Efficiency Scheme, will include household names such as Sainsbury’s, Tesco, Marks & Spencer, John Lewis, Barclays, HSBC, Hilton and Marriott. It will also include manufacturers and construction companies, for example Procter & Gamble, Unilever and Balfour Beatty. These businesses will be ranked according to reductions in energy use and improvements in energy efficiency alongside public sector organisations such as NHS trusts, local authorities and government departments.

Analysis for the Environment Agency suggests that the scheme could reduce CO₂ emissions by up to 11.6 million tonnes per year by 2020 - the equivalent of taking four million cars off the road. It is also expected to save organisations money through reduced energy bills – benefiting the economy by at least £1billion by 2020.

More than 20,000 organisations will have to register with the Environment Agency by the end of September this year. Around 5,000 of these organisations – those that used at least 6,000 Megawatt hours (MWh) of half hourly metered electricity in 2008 – will have to report their emissions and, from 2011, buy allowances for every tonne of CO₂ they emit. During the introductory phase in 2011 and 2012, allowances will be sold at a fixed price of £12 per tonne of CO₂.
All the money raised from allowance sales will be recycled back to participants according to their energy performance. The best performers will get more money back than they paid, while poor performers will get less. From next year, the Environment Agency will publish an annual league table highlighting the best and worst performers in CRC.

From 2013 a cap and trade system will be introduced. This will limit the total amount of carbon dioxide these organisations can emit by capping the total number of allowances available and selling them at auction.

A further 15,000 organisations that use less than 6,000MWh, but still have at least one half hourly electricity meter, will be obliged to register and declare their electricity use.

Tony Grayling, Head of Climate Change and Sustainable Development at the Environment Agency said: “The CRC Energy Efficiency Scheme is an opportunity for organisations to do their bit for the planet and save money. "The league table is a very public judgement on how seriously you take your environmental responsibilities. If organisations don’t take up the challenge, there is a risk to their reputation and their pockets.”

The biggest CO₂ savings are likely to come from hotels, restaurants, retail and the public sector. For the majority of these organisations, better management of heating, lighting and computer systems will yield quick results.

“Carbon reduction doesn’t need to be complicated or expensive,” says Tony Grayling, “There are simple and inexpensive steps every organisation can take to cut their energy consumption – from motion sensors for lighting in offices to higher efficiency motors in manufacturing.”

Organisations that qualify for CRC must register for the scheme with the Environment Agency by 30 September 2010.

Source: Environment Agency Website (www.environment-agency.gov.uk) – 10 April 2010
NEW PROTECTION FOR WORKERS FROM ARTIFICIAL LIGHT

New regulations further protecting workers from the dangers of hazardous sources of artificial light come into force today.

The Control of Artificial Optical Radiation at Work Regulations meets a European Union Directive to ensure that standards are set and harmonised across Europe to protect workers from harm arising from exposure to hazardous sources of artificial light.

Some sources of artificial light, particularly UV radiation and light from lasers can harm the eyes and skin of workers and must be properly managed.

Workers in Great Britain are generally well protected from dangerous sources of light and the majority of businesses know how to manage the risks effectively. Therefore the regulations will mean few practical changes for most businesses, including those who are already managing the risks.

To help those businesses who are not already managing the risks understand what’s required and what they need to do, HSE is producing guidance to ensure workers can remain appropriately protected.

Common sources of light in the workplace such as office lights, photocopiers and computers are not affected by the regulations.

Source: Health and Safety Executive Website (www.hse.gov.uk) – 27 April 2010
Readers were informed in the Winter 2009 edition of the Vitreous Enameller that The CEN/TC 262/WG 5 Committee have been liaising with steel standards committee ECISS/TC 13/WG 2. The steel standards committees have recently been restructured and ECISS/TC 13/WG 2 has been replaced with committee ECISS/TC 109/WG 3. Mr Andrew Friend of STI/36 has led in the drafting stage for a two-side enamelling part of the proposed hot rolled steels standard. The draft standard has been submitted to the steel standards committee and the matter will be discussed further at the ECISS/TC 109/WG 3 meeting on 27th May 2010 in Paris.

Recent systematic reviews of international standards identified that the abrasion standard ISO 6370-2:1991 contained reference to obsolete standards for steel balls and grit. The matter is being discussed with ISO/TC 107 and was also discussed at the recent CEN/TC 262/WG 5 meeting in London. It was agreed that the topic of abrasion will be developed further with a Germany/UK lead so that ISO 6370-2 can be amended appropriately.

STI/36 have been informed of a new work item proposal from Italy on the effects of material on water quality. This is a complex area and has been discussed between the European Community for a significant number of years. The matter was discussed at the recent CEN/TC 262/WG 5 meeting in London as the enamelling community need to influence the construction products community. It is essential that adequate and correct reviews are conducted on enamel as a material to demonstrate that water in contact with enamelled surfaces is not harmful for human consumption. Further work is required and will be led by CEN/TC 262/WG 5.

The merger of the standards ISO 2746 and EN 14430 is progressing and STI/36 will take an active interest as two major UK manufacturers make considerable use of this test.
The following British Standards Publications are due for review:

- BS 3831:1964 Specification for vitreous enamel finishes for domestic and catering appliances
- BS 4900:1976 Specification for vitreous enamel colours for building purposes
- BS 7957:2000 Vitreous enamel systems. Determination of self-cleaning properties

The deadline for voting is early July 2010 so if you have comments on any of the above standards I would be grateful if you could contact the IVE please.

Please continue to forward details of any standards related questions or queries you have to the IVE.

SAQLAIN ALI
Chairman STI/36
IVE Council Member

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Vitreous enamels are similar in composition to ceramic glazes in the sense that they are both glasses with random structures which give rather indefinite lines in X-ray spectra and hence we are unable to say with certainty what compounds are present except that they are complex silicates and borates.

While ceramic glazes can be fired for several hours, since the substrate is stable to heating, enamels must be fired in a matter of minutes to avoid excessive oxidation of the base metal and warping. This means that numerous chemical reactions between raw materials in the enamel must have been carried out in the pre-firing or fritting operation, whereas with ceramics these can often be allowed to proceed in the actual glost fire. In enamelling, the fritting operation is of vital importance and the resulting preparation of enamel is a matter of grinding the frit and adding clay as a suspending agent, together with small amounts of electrolytes and in some cases binders to improve the biscuit strength.

Clay is a compound of alumina and silica, both of which raise the firing temperature required for the frits. Hence, the amount that can be used is limited; commonly 7-10%. In some cases where the effect of clay on maturing temperature is not permissible (as with low temperature enamels such as those used for alumina), finer grinding is used and small amounts of colloidal material added, i.e. silica gel. The function of the clay is to act as a suspension agent. The original one was Vallendar clay, a very plastic material found in Germany. When the wars cut off supplies of this, other materials had to be utilised such as china clay and some ball clays, and these are used today very widely. Before proceeding further, let us consider the formation and extraction of these raw materials as this gives some insight into their properties and uses.
In this country there are two main sources of white burning clay – china and ball clays. There are many others burning to off-white, tan and red colours, some of which have limited use in dark enamels such as ground coats. The bulk of the supplies of china clay come from Cornwall, principally around St. Austell. It is supposed to have resulted from the decomposition of the local granite by hot volcanic gases in the geological past and to have remained in situ. Geologists refer to it as a primary clay to distinguish it from secondary clays which have been transported by water and laid down in lakes or estuaries. Ball clays are secondary clays and there are deposits of secondary kaolin in America and other places but not in England.

To extract the china clay the normal process is to dig a hole and then wash down the sides with a powerful jet of water. This brings down a mixture of sand, rock and china clay which is collected in a sump. From this is pumped the clay slurry mixed with mica and fine sand. The coarser material is elevated to form the well-known spoil heaps, some of which are now being used for making concrete. About 10% of the material mined is clay. The slurry pumped out of the pit is then allowed to settle to remove sand and mica and is finally run off to a collecting point station where several clays may be blended in slurry form before de-watering in a filter press. The press cakes may contain about 25% water and they are finally dried in oil-fired driers and pulverised. The material is then either bagged or loaded bulk into shops. The paper trade is the largest consumer. Clay used for enamelling is a very minor percentage of the total.

The extraction of ball clay is a very different procedure. The ball clays were laid down in the main areas in England as a result of the decomposition of granite by weathering and subsequent transport of the clay by streams and rivers. The clays were deposited in inland lakes in the case of the Newton Abbot deposit in the Bovey Basin and in the Meeth deposits in Devon, and possibly in an estuary in the case of the Dorset clays. Those in North Devon and Dorset tend to be tough and burn to a rather creamy colour, while the South Devon clays are whiter burning. There are vast deposits of clay here. At Bovey alone there is an area nine miles long by almost three wide and the depth is unknown – one company is 400 feet down at present.

Deposits of clay laid down in lakes and estuaries have interesting features. The climate was tropical at that time and rainy seasons alternated with dry
ones. In the former the rivers in spate brought down stones, clay, sand and vegetation which formed a layer to be covered with finer clay in the drier seasons when the rivers were more gentle. Subsequently the whole was compacted and the vegetation changed to coal-like material such as lignite. When these deposits are exposed by open cast mining a succession of clay seams is revealed separated by beds of sand and pebbles or bands of lignite. This makes it easy to follow the various seams and extract them.

The over burden is normally removed by bulldozers and scrapers and taken then well away from the clay face to avoid possible contamination. The seams are then worked by pneumatic shovels or in favourable circumstances by machines like coal cutters. When there is a heavy demand for a particular type of clay it may be exploited by deep mining, especially where dips in the seams would make it possible to move all of the clays above. Here the practice is to sink a shaft and work outwards from this in the normal methods for coal mining. The clay extracted is taken to bunkers under cover where it is allowed to dry off somewhat. If it is to be blended it is fed into a shredder and the pieces thrown up on to a heap by a rotating belt. The blending can be done in any desired proportions by mixing the raw clay in the shredder. For some purposes the clay is dried and pulverised in an Atritor giving a fine powder which will pass about a 300 mesh sieve. Other varieties are pelleted clay and, of course, the ordinary lump or ball clay. For enamelling the pulverised, dry clay is probably convenient to use. There is a large variety of ball clays available, varying from siliceous stoneware type, suitable for making clay pipes, to the finest white burning clay for fine pottery. By its nature and method of extraction china clay is purer than ball clays and it is also more expensive.

Whichever clay is used in enamels the purpose is to promote suspension. Left to itself in a liquid, a powder will settle according to Stoke’s Law.

\[
V = \frac{2}{9} \frac{gr^2 (D - d)}{\eta}
\]

Where  
V = velocity of falling particles in cm/sec  
D = S.G. of particles  
d = S.G. of liquid  
r = particle radius in cm  
\eta = viscosity of liquid  
g = accumulation due to gravity
Since frit is not normally ground to superfineness, $r$ tends to be relatively great and $D$ is of the order of 2.5-3.0, while water $d=1$. If the velocity of settling of frit is compared say with the very fine particles of clay, it is found to settle much faster. The clay added contains a proportion of particles of sub-microscopic size, i.e. colloidal particles. These are negatively charged in water which means that the particles tend to repel each other and prevent the formation of aggregates which would tend to settle. In addition clay particles can swell in water and form a structure in which the frit particles find it difficult to settle at anything like their normal rate.

A further point is that by the addition of small amounts of electrolytes the charge on the clay complex can be partly neutralised. This means that the particles no longer repel each other to such a great distance and the point comes when they form aggregates often trapping liquid, and forming a loose viscous structure which again prevents settling of frit. A similar action occurs if colloidal biscuit strengthener is added followed by electrolyte.

The control of viscosity is also important for spraying and dipping, particularly the latter. It can be shown that the amount of material taken up on dipping depends on the viscosity and pint weight (or specific gravity) of the slop enamel. At a constant S.G. the take-up is proportional to the viscosity. It is therefore important to control this before use. This is where the electrolyte addition at the mill comes in.

The normal checks in slop enamel are therefore:

(1) The sieve test after grinding.
(2) The specific gravity (or pint weight) for solids : water ratio.
(3) The viscosity or consistency test.

The last test can be done in a viscosity tube where the rate of flow of the slip enamel is measured as it passes through a $\frac{1}{8}$” diameter hole in a 1” diameter tube filled to a constant height at the start. This is a good, simple routine test. A rather more sophisticated test is to use a burette connected to a capillary tube. The time for 10cc’s to flow is taken at various intervals down the tube and the applied force is taken as the mean vertical height of the liquid column during the measurement. This is plotted against rate of flow in cc’s per second. (See figure 1).
The Gardner Mobilometer

This is a variation of the previous method. A loaded plunger is allowed to sink into a column of enamel and the time to sink 10cm is noted (see figure 2). Weights are varied and the total weight (including that of the piston) is plotted as force against rate of travel.
The dipped plate

A useful check used to control the amount of uptake is the dipped plate method. The test plate is a 1-2 sq ft in area and can be flat or cylindrical. It is ground coated, dipped and drained in the vertical position. The weight of uptake is then measured wet and compared with a standard.

It will be obvious clays used for enamelling should not contain impurities which affect the colour of the fired enamels, e.g. a yellow burning clay would not suit a white enamel. Equally impurities likely to burn out and give pinholes are to be avoided.

In the Bulletin of the Institute of Vitreous Enamellers in 1959[1] the I.V.E. recommended certain control tests for ball clays used in enamel.

1. A 5lb sample was taken and pulverised and dried as 110°C.

2. The viscosity of a sample of 70 grams in 1,000 grams of distilled water is determined by viscosity tube or torsion viscometer. Variations from standard in this test are probably due to soluble salts (usually sulphates) and colloidal silica. It was also recommended to take thixatropy on the torsion viscometer after standing 2 mins.

3. Empirical test for impurities: 100 grams of clay are agitated with 4 litres of distilled water containing 0.25 Na₂CO₃. The slurry is passed through a 200 mesh sieve and the residue washed under a tap, dried and weighed. It is then examined under a microscope for black specks, fibres, lignite or magnetite. The residue is mixed with 50cc’s of white cover coat enamel and sprayed on to a ground coated panel approximately 8”x10” and fired under standard conditions against a check sample. The specimen should show no blisters and not more than say five black specks, although the number is a matter of opinion.

4. Pick-up value: In this test batches are made up substituting quartz for frit and adding no electrolyte.

   a) For cover coats: 1,500g quartz through 200 mesh )
      105g clay )
      990ml water )
Grind for 15 mins in small mill and adjust S.G to 1.6. Two weighed ground coated sheet plates with 1/4” hole for draining on hooks are dipped, suspended vertically for 1 min, dried at 110°C and re-weighed. The weight of dry enamel taken up in grams per sq ft of plate (both sides) is then calculated.

b) For ground coat enamel clays: 1,500g quartz – 200 mesh )
   75g clay )
   990ml water )

Proceed as before.

(5) Colour test: 1000g milling of titania enamel is taken and sprayed on to three plates to a controlled application weight. One plate is fired at the control temperature, the others being fired at 10°C on either side of the control temperature. The colours are then compared with a standard.

(6) Other tests: Include a loss on ignition test in which 1 gram of dried clay is ignited in a platinum crucible and the weight loss is measured. Acid resistance test: Done by some manufacturers on standard enamel using different clay samples but it is not felt that this test is justified.

REFERENCE

REFRACTORIES IN A GLOBAL GLASS MARKET

The world tonnage of refractories in 2007 was estimated at around 34 million metric tonnes and this is expected to rise to around 42 million metric tonnes by 2010 with increased market value and good profit potential[1].

Recent years have seen significant changes in supply of refractory materials to industries worldwide. In the next 2-3 years, particularly for the glass industry, Chinese refractories for example, will be sold in India, South East Asia and parts of Europe[2] and European companies now have manufacturing facilities in this part of the world.

As a result of this glass producers have a much wider choice of refractory sources now and competitive pricing makes these new refractories an attractive option[2].

Many manufacturers are learning to close the quality gap between materials sold on the domestic market and export products[2] and may do so in a relatively short time calling on lessons learnt from other areas of the world as they went through the same process.

It is still extremely important however to carefully assess the widening range of refractory materials for the glass industry to ensure that they give the performances required for cost effective, long term glass production.

This paper looks at some of the methods to assess critical service performance of materials for glass making applications and highlights the potential impact on glass production should refractories not perform to the required standards.
First of all we will look at some figures for refractory usage across high temperature industries. Figure 1 (page 26) shows that the worldwide steel industry still dominates the demand for refractory materials consuming over two thirds of the world’s refractories. In comparison the glass industry consumes a relatively small portion of refractories annually at around half a million tonnes.

As Figure 2 (page 26) shows, this annual consumption of refractories by the glass industry amounts to total sales value of 0.4 to half a billion pounds of which fusion cast glass contact refractories represent around 45%, followed by basic refractories such as those used in regenerators.

Overall however these sales represent relatively small proportion of the total annual world market value. Nevertheless glass producers still demand high quality refractories for their furnaces to improve life and hence reduce manufacturing costs.

World glass production in float, container, fibreglass and specialty areas currently stands at around 100 million tonnes per annum (Figure 3, page 26). All figures exclude China, however a 2005 estimate suggested that float glass production stood at around 20 million tonnes, 50-60% of the rest of the world. There are 300 float lines in the world and half of these are in China.

Around 5 kg of refractories are consumed per tonne of glass produced and the cost of these refractories is approximately £5 per tonne of glass produced. The cost per tonne of glass is equivalent to 2% per tonne of yield. Refractories are therefore normally the largest single component of furnace build and repair costs.

Their performance can influence furnace output and product quality and hence process economics. The deterioration of the refractories determines the life of the furnace and, as consequence, the lining repair schedule. These materials are therefore an essential component of the glass making process where they are key contributors to business success.

Figure 4 (page 26) shows some of the important areas in terms of performance.
Figure 1: REFRACTORIES – THE GLASS INDUSTRY MARKET

Figure 2: REFRACTORY SALES TO THE GLASS INDUSTRY

Figure 3: GLASS INDUSTRY SECTORS

Figure 4: GLASS FURNACE WEAKNESSES
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Figure 5: EVALUATION OF CORROSION RESISTANCE TESTS

Figure 6: DYNAMIC TEST, 1550°C, 24 HOURS, AZS, FLOAT GLASS

Figure 9: EXUDATION PERFORMANCE

Figure 10: BLISTER TESTS: FUSION CAST AZS
The glass contact regions namely the side blocks and throat (of container glass furnaces) shown here are the most vulnerable areas of the furnace as glass corrosion is at its most aggressive here.

For most furnaces these critical regions are most likely to be life determining, so it is extremely important to correctly evaluate resistance to high temperature corrosion.

There is an endless list of tests available for the assessment of refractories in contact with molten glass. This variety of tests can be divided into static or dynamic tests. In static corrosion tests, the refractory specimen is fixed in position via a cement position allowing no specimen movement in the molten glass. In dynamic test there is continual movement of the specimens in the molten glass. Static tests are useful for comparing the relative performance of glass contact materials however for critical, furnace life limiting applications a ‘dynamic test’ is preferred.

At ambient temperature the glass cullet is placed in platinum crucible and the furnace is then closed and heated. At test temperature samples are lowered into glass for testing. Assessment of corrosion is by measurement of change in volume.

This test more accurately reproduces the type of glass line and other high wear corrosion experienced in furnace operation. Corrosion is often ten times higher at a triple interface, such as the glass line, than in other regions of the furnace.

Figure 5 (page 27) shows the performances of three fusion cast refractories in soda lime glass. As can be seen the dynamic test more accurately reproduces the enhanced corrosion at the glass line and other high wear areas seen in service.

The rotation of the samples during the test prevents the formation of a protective boundary layer at the glass/refractory interface, which, in operating furnaces normally only forms in areas of quiescent or stagnant glass flow. The formation such boundary layers in the static corrosion test can restrict its application. The static test can be used for simple comparisons, but dynamic tests correlate much more closely with in service performance as shown in the graph.
Accurate corrosion assessment is therefore extremely important when selecting new glass contact refractories. What is also important for AZS (Alumina-Zirconia-Silica) materials, because of their varying composition within a block, is to compare pieces from similar locations within the blocks.

Figure 6 (page 27) shows the variation of corrosion volume loss with temperature. At 1550°C three AZS materials D, E and F were compared using the dynamic corrosion test. From datasheet values the materials appeared similar however Material F gave a higher than expected volume loss at 47%, the reason for which was then investigated further.

Further analysis (Figure 7) showed that Material F contained the highest percentage of non AZS components in the glassy phase at around 8%, compared to values of just over 7% for material E and just over 6% for material D.

Material F also had the least refractory glassy phase composition. The glassy phase is overall the least refractory component of AZS materials and the route through which chemical attack takes place.

As well as considering corrosive effects of glass on the wear of the glass contact refractories we must also consider the potential impact of the corroded refractory on glass quality. A significant source of glass loss can be attributed to solid, vitreous and bubble faults originating from furnace refractories.
THE VITREOUS ENAMELLER

Figure 8 shows the typical data sheet information for a new 33% zirconia AZS fusion cast material that was being considered for use in a container glass furnace. This data is comparable to other similar products available on the market and from the data its performance would be also expect to be comparable and nothing untoward would be expected.

<table>
<thead>
<tr>
<th>Chemical Analysis</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>49-50</td>
</tr>
<tr>
<td>SiO₂</td>
<td>&lt; 15</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>34-35</td>
</tr>
<tr>
<td>Alkalis</td>
<td>&lt; 1.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density, g/cm³</td>
<td>&gt; 3.4</td>
</tr>
<tr>
<td>Apparent Porosity, %</td>
<td>&lt; 2.5</td>
</tr>
</tbody>
</table>

However when assessed for high temperature glassy phase exudation by firing to 1500°C in air and measuring volume changes you get a bit of a surprise (Figure 9, page 27).

The material (H) gave higher than expected values for exudation above the acceptable level for this type of material. The exudate is shown on the surface of the test sample. A result below the maximum acceptance limit of 2% for superstructure material was expected, but measured results gave values in excess of 4% and above the acceptable limit leading to increasing risk of glass faults.

As is well documented the difference in exudation performance relates to the extent of oxidation of species within the AZS refractory during its manufacture. A poorly oxidised material has the potential to produce high exudation.

Use of this material in the proposed application could have a catastrophic effect on glass quality during the initial stages of furnace operation and increasing the risk of glass defects such as crystalline, dendritic zirconia faults in the finished product.
Assessment of blister formation, derived from impurities such as ferric oxide in AZS materials is also important because of the impact on glass quality. This involves firing of a refractory disc in contact with glass and assessing by microscopy the number of blisters/cm² at the glass/refractory interface.

Figure 10 (page 27) shows two materials, I and J that were assessed.

Material I showed low blister formation. Ideally low single figure values are acceptable. However the high blister count at around 35 /cm² would make this material unsuitable for use.

In addition to assessing the performance of glass contact refractories and their effect on glass quality, careful assessment of materials in other regions is essential to ensure smooth, continuous operation.

Figure 11 shows the typical data for silica which was used in the crown of a float furnace.

<table>
<thead>
<tr>
<th></th>
<th>Current Silica</th>
<th>New Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ %</td>
<td>95.8</td>
<td>96.0</td>
</tr>
<tr>
<td>Al₂O₃ %</td>
<td>0.58</td>
<td>0.54</td>
</tr>
<tr>
<td>Fe₂O₃ %</td>
<td>0.85</td>
<td>0.9</td>
</tr>
<tr>
<td>CaO and MgO %</td>
<td>2.25</td>
<td>2.31</td>
</tr>
<tr>
<td>Na₂O and K₂O %</td>
<td>0.20</td>
<td>0.5</td>
</tr>
<tr>
<td>Bulk Density, g/cm³</td>
<td>19.7</td>
<td>20.8</td>
</tr>
<tr>
<td>Apparent Porosity, %</td>
<td>1.82</td>
<td>1.78</td>
</tr>
<tr>
<td>CCS, MPa</td>
<td>34.1</td>
<td>32.5</td>
</tr>
<tr>
<td>PLC @ 1600°C, %</td>
<td>0.3</td>
<td>0.35</td>
</tr>
</tbody>
</table>

*Figure 11: SILICA REFRACTORY FOR FURNACE CROWNS*
As we can see the chemical and physical properties of the new material, are generally similar to the currently used silica product. So from the data sheet no surprises are apparent.

However during the heat up of the furnace the crown expansion grossly exceeded expectations making control difficult and resulting in the distortion of the crown and opening up of longitudinal joints along the crown. Potentially these could lead to long term maintenance issues and glass quality if alkali condensation causes rat holing in these joints.

The expansion curves of the two materials in Figure 12 clarify the observations. The curve for the current product is typical of high quality crown silica. However the new silica continued to expand as a result of under firing and therefore high levels of unconverted quartz remained.

So when selecting new products and for quality control purposes it is important to test critical in-service properties. Although silica is relatively cheap compared to the fusion cast glass contact refractories, it is still critical in terms of furnace operation, furnace life and glass quality.
Another critical performance area within float glass furnaces over the years is the tin bath. Today around 95% of the world’s flat glass is produced by the float process and this area has its own critical set of performance indicators.

In particular the performance of tin bath bottom blocks is extremely important. The majority of bath blocks are produced from alumino silicate fireclay. A variety of issues have been observed in this area of the float furnace over the years. Nepheline peeling is the most common problem still seen today. Formation of nepheline leads to volume expansion and thermal expansion mismatch which leads to detachment of material.

Alkali penetration tests were carried out on three materials over an extended period and following this the degree of penetration is assessed either visually or by microscopy.

Another issue in tin baths is bubble formation on the surface of the glass due to thermal transpiration of blocks when mean pore diameter is smaller than diameter of gas molecules.

This is characterised by the hydrogen diffusivity test and examines the pressure build up in mm H$_2$O in samples of bath block. A cut off level of 150mm H$_2$O is used. It is also important to examine different areas of the block as diffusivity may vary.

The corresponding values of materials K, L and M are shown Figure 13.

<table>
<thead>
<tr>
<th>Material</th>
<th>Alkali Penetration $800^\circ$C - $1000^\circ$C 7 days</th>
<th>Hydrogen Diffusivity mm H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>No</td>
<td>57</td>
</tr>
<tr>
<td>L</td>
<td>No</td>
<td>142</td>
</tr>
<tr>
<td>M</td>
<td>Yes</td>
<td>6</td>
</tr>
</tbody>
</table>

*Figure 13: ALKALI PENETRATION / HYDROGEN DIFFUSIVITY*
As with many refractory materials a balance of properties is required to optimise performance.

Figure 14 aims to show the inverse relationship between permeability (i.e. risk of alkali penetration through LARGE pores) and H$_2$ diffusivity (i.e. risk of H$_2$ transpiration through SMALL pores.) This is the curved line. The area of ‘acceptable’ balance between these 2 parameters (which can only be defined by experience) is within the square shown.

Recent studies$^3$ have indicated that the amount of glassy phase in the block plays an important role as to whether peeling occurs as a result of nepheline formation. So assessment of the glassy phase should also perhaps be carried out when selecting new bath block refractories.

In addition to assessing the performance of increasing numbers of fireclay bath blocks on the market, a new generation of calcium aluminate blocks is now available on the market. (Figure 15), hence more choice still for the glass maker!

So there are many new refractory opportunities for glass producers, but it is critical to assess the in-service performance of the ever increasing choices of materials available on the market as data sheets can only provide a limited amount of information. Independent evaluation provides the benefit of improved confidence to the glass manufacturers, for refractory producers and furnace engineers alike.
REFERENCES


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