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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 2009

Just when you thought that you had got rid of my editorials, I have come back. Believe it or not, the last one I did was for the Summer 2004 edition. Then the words just used to flow out regularly as clockwork once every three months. However, this one has proved much more of a challenge. When I offered to do it for Mark, he gave me the usual deadline and I thought - “Oh yes no problem - plenty of time”. It is now two days to go and I still haven’t finished it. Well truthfully I haven’t even started it, apart from the writing plan which I did about three weeks ago. My offer to do it came as the result of an IVE executive meeting. An elected group of us meet regularly to resolve urgent issues which cannot wait for the next Council meeting, which might be many months away. Inevitably some things get missed at Council and the writer of the editorial for the next journal was just one of those. The other three members of the executive had done one fairly recently and so I offered my services. So here I am and what do I say? I could go back to the old faithful and talk about my railway modelling – “Oh not again”, I hear you say. Maybe the weather? Or perhaps I should actually talk about the IVE.

Among other things discussed at that meeting was the work that the IVE and its council members do for the membership, which may not be immediately obvious. There are Council members who chair both national and international standards committees. There are others who regularly attend these committees and contribute to updating and preparation of new standards. The IVE always has been at the forefront of ensuring that standards relating to vitreous enamel are good and workable. Occasionally one has been slipped through by a committee which does not understand our unique material and does not call on our representatives - they usually get it wrong. So, where possible, we try to ensure that where vitreous enamel is, or is likely to be, the subject of a standard that we have representation on the relevant committee. This usually depends on the dedication of individuals and the goodwill of their company. A few hard working council members take on this responsibility in addition to their normal company workload. We even have retired members attending committees. For these latter, the IVE does all it can to support them financially so that they are not out of pocket. All of them are dedicated to ensuring that the standards and test methods for vitreous enamel which you, our members, have to adhere to are workable and practical. In addition to standards
committees, our members attend Health & Safety and Environmental meetings which have direct access to Government and are fully recognised. This ensures that the excesses of legislation can at worst be mitigated and at best be changed. You receive regular reports in this journal on the latest news on all of these subjects. So what am I getting at? – Three things. Firstly, if you have a particular sector which is not well represented on standards committees - and enameled cookware and holloware comes to mind – please contact us. Secondly, if you feel that you would like to have a personal input to standards – please contact us. And thirdly, please support us through membership. The only way to be on these committees is as part of IVE – you cannot be a personal representative.

The working group looking at the future role and structure of the IVE have met with a number of related Institutes to pick their brains, to look at forms of collaboration and to generally find out what is going on around us. There is a general groundswell from everyone that we have talked to, that whatever else, we should talk to each other more, so that we can help each other and learn from each other’s experiences. In the longer term we may build up a much closer relationship with one or more of them, but we are taking our time to look at what is right for our Members. Our membership structure, having a combination of both companies and personal members needs protection. Over the years both of the types of member have shown individual benefits to the running of the IVE. But please be assured we will not do anything without the full support of our members. I hope that you all agree that talking with these other bodies can give nothing but benefits. Our Chairman, Simon Cook, has held some very interesting discussions with the two Craft and Art related Institutes, and despite the fact that they are in a totally different “market”, their aims and aspirations are very similar to ours.

Running the technical support helpline for IVE has always been an interesting experience. Whilst we do receive genuine technical queries, often about uses of vitreous enamel which are novel and sometimes thoroughly impractical, the majority of enquiries are from the general public and are “how do I clean it?,” particularly about baths. Chris Taylor and I have been building up an enormous amount of knowledge about what people do to baths in their frantic attempts to keep them clean. The worst problem which seems to occur in a bath is the formation of an extremely tenacious layer of what people loosely refer to as “limescale”. The layer is a hard semi transparent light beige film which seems to form as a result of reaction between soaps (in the generic
termand water hardness. It is not limited to hard water areas as if there is any calcium and magnesium water hardness present, this film will form and gradually build up. By time that it is visible, it is extremely difficult to remove. It is chemically neutral, so the vinegar cleaning method does not work. Some success can be achieved using white spirit, but it is still a very “elbow grease” intensive process. The answer is very simple, but most of the people I talk to are frankly horrified when I tell them what to do. The key is to dry your bath every time you use it. This removes the water left on the surface and probably removes the film which is forming. You would think I was asking them to paint the Forth Bridge!! A famous actress allegedly said when told to do this – “I would rather not have an enamel bath than to have to dry it each time I use it”. All I ask is to get an old towel and wipe it over – I timed it this morning – less than half a minute! Worse still, we have had people who have used phosphoric acid, hydrochloric acid, limescale remover and a well known cleaner with “bang” in the name. Then they ring us and ask why the enamel is not glossy any more and can we please help – what can they do about it? I rest my case!!!

Angela has asked me to include a plea to those members who have not renewed yet - please send your remittance as soon as possible. Members will have been advised that we have recently changed the user name and password for the Member Zone of the Website. This zone is useful in providing you with readable files of back issues of the journal and an ever growing range of other useful information. The user name and password will be changed again on 1st July 2009 and will then only be supplied to renewed members, so if you want to maintain contact with this increasingly useful part of the Website, please ensure that your membership is up to date. I am currently putting together the next batch of useful information to go on to the Zone, so if there is anything which you feel would be of value to you or your company, please ask and I will try to accommodate your needs. That is what we are here for. For company members, if you have not renewed by this date your company will also be removed from the member’s services list along with all other references.

Hopefully it won’t be another six years before you hear from me again, or perhaps you would prefer that!

MIKE COLLINS
President / IVE Technical Support
INSTITUTE NEWS

IVE WEBSITE – MEMBERS’ ZONE

Please note that passwords and usernames for the Members’ Zone of the IVE website have recently changed.

If you have not received notification of the changes and are a member of either the IVE or VEA and want to access this service, please contact Angela Nutting for a password and username on +44 (0)1543 450596 or at info@ive.org.uk

The Members’ Zone:

- News & Diary Dates
- AGM Meeting Agendas & Minutes
- Standards & Specifications for VE
- Index to Archives
- Design of Parts for VE
- Publications, inc. ‘The VE’

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EVENTS CALENDAR

21 June 2009 - 25 June 2009

11th International Conference and Exhibition of the European Ceramic Society
Venue: Cracow, POLAND
Contact: Krzysztof Haberko
Tel: +48-12 617 2307
Web:www.symposium.pl/
Email: haberko@agh.edu.pl

25 June 2009 - 05 July 2009

JIHAZ MANZIL 2009 - International Exhibition of Electrical Appliances, Kitchen, Decoration and Arts of Cooking
Venue: Casablanca, MOROCCO
Contact: OFEC (Office des Foires et Expositions de Casablanca)
Tel:+212 (0) 522 20 06 54
Web:www.ofec.co.ma/
Email: foire@ofec.co.ma
THE VITREOUS ENAMELLER

BUSINESS NEWS

EAST ASIAN COUNTRIES EMERGING AS NEW DESIGN “POWERHOUSES”

East Asian countries such as Korea and Singapore are beginning to shift their economic emphasis away from low-cost production and into design, new research suggests. The findings, which appear in a new report examining international design capabilities, could have significant implications for the UK, where high-value activities such as design are regarded as essential to future competitiveness.

The “International Design Scoreboard” has been produced by a consortium of UK universities led by the University of Cambridge and supported by the UK Design Council. It marks the first ever attempt to compare national design capabilities and will be published on April 15th 2009. The project has been funded by a research grant over £300,000 from the joint Arts and Humanities Research Council (AHRC)/Engineering and Physical Sciences Research Council (EPSRC) research programme ‘Designing for the 21st Century’.

A total of 12 countries are assessed based on a series of indicators, including numbers of design graduates, and the strength of the design consultancy sector. The results suggest that western nations are under increasing threat from emerging East Asian “powerhouses” as they develop their design sectors, invest in national design promotion and produce skilled design graduates.

If their ambition is successful, countries such as Korea will become even more competitive in areas such as design. They will also have the added advantage over many Western countries of a close production base, which in many cases has already shifted to the East.

Britain is currently recognised as a world leader in design. Design consultancies have an annual turnover of around £4bn and the design industry as a whole has a value of around £11.6bn. The consultancy sector directly employs nearly 62,000 people, with many more designers, perhaps twice this number, employed in industry. Overall, the sector is regarded as integral to the country’s future competitiveness and economic prosperity.
“The study is an imperfect first attempt to rank countries’ design performance, but its overall results, which show that the design sector is growing in the Far East in a manner which outstrips many Western countries, are consistent with anecdotal evidence,” Dr James Moultrie, from the University of Cambridge’s Institute for Manufacturing, said.

“East Asian nations which have traditionally competed on price and low labour rates are now increasingly competing through design as well.”

The research measured design capability according to seven indicators: (1) public investment in design, (2) total number of design graduates, (3) number of World Intellectual Patent Office (WIPO) design registrations, (4) number of WIPO trademark registrations, (5) number of design firms, (6) turnover of design services sector and (7) employment in the design services.

Data was collected from a variety of sources, including national statistics agencies, published surveys and reports, and national design support bodies.

Each indicator was assessed in both “absolute” and “relative” terms, in order to determine both the scale of a nation’s design capability and the intensity of design as a proportion of the economy. For example, total public investment in design promotion and support was measured alongside that investment as a percentage of Gross Domestic Product.

Unfortunately, reliable and comparable data was not available for a number of economies with a strong design emphasis, such as Germany and China. The 12 nations for which sufficient data was available were ranked both on their “absolute” and “relative” results. An average of their scores provides some sense of which countries are the best performers.

The study ranks the UK 4th in absolute and 6th in relative terms. The UK retains its leading capabilities in design education, but the report raises concerns about a decline in both turnover and employment in the consultancy sector. Data suggests that the UK design services sector was adversely affected by the dot-com crash in 2001 and it may be that the sector will be further affected by the current economic climate. However, overall design employment appears to be rising, according to official DCMS figures.

Perhaps unsurprisingly, the US ranks 1st overall in absolute terms. But it is South Korea that is emerging as a new design powerhouse, ranking second in
both absolute and relative terms. Singapore ranks 1st in relative terms, suggesting a high intensity of design activity relative to the size of the nation.

In both Korea and Singapore, sustained public investment is enabling the design sector to flourish, as evidenced through a growing number of design graduates and registration of trademarks and designs.

“While this study does not directly identify any clear link between the location of production and design, there is no doubting the desire of Korea and Singapore to build on their production base and develop their design capabilities,” Dr Moultrie added.

The report acknowledges that data is currently sparse and difficult to compare, meaning that any international comparison needs to be treated with care. It also lays out a proposal for a more reliable set of indicators, which will form the basis of future work.

In particular, no data was available for how much firms spend on design. The project team also teamed up with the UK Design Council to conduct an exploratory survey of design spend in UK firms.

From a firm’s perspective, any spend on design is future orientated, whether it relates to the creation of products and services, the promotion and communication of offerings or the development of corporate identity. This original study demonstrated the viability of capturing data relating to such spend in firms.

Initial estimates indicate that UK firms spend around £50bn on design annually. Of this, around £40bn is spent on design relating to the technical and engineering aspects of developing new products and services. This compares with private sector R&D spend at around £21bn. This high technical design spend in comparison with R&D is surprising, and further work is required to validate this value.

Spend on non-technical design, such as the user experience of products and services, promotion and corporate identity is in the order of £10bn, with 50% of this outsourced. These early results are based on a small sample 358 companies that are representative of UK firms. A separate report outlining these findings will also be published on April 15th 2009.
A follow-up project is now being planned which will collate data for a wider range of nations to produce a more comprehensive set of international rankings.

David Kester, Chief Executive of the Design Council, said: “For policy-makers to take concerted efforts around the application of design, we need strong evidence and common metrics. Over many years, the Design Council has carried out its own research and provided economic evidence that has informed the UK government’s understanding on design.

“This report will add to the national evidence base on design and its role in the economy. It provides us with new methodologies to test and over time could add significantly to our common understanding of design in industry.”

Professor Philip Esler, Chief Executive of the Arts and Humanities Research Council, AHRC, said: “In the 19th century a deliberate and far-sighted investment in design made a major contribution to Britain’s leading role in the Industrial Revolution. In this era of the Digital Revolution, design will be just as, if not more important.

“For Britain to rise to this challenge, it needs accurate measures of its performance relevant to competitor nations. This project, embracing science, engineering and the arts and humanities in the UK’s integrated research base, represents an important means to this end.”

The complete Design Scoreboard report, entitled International Design Scoreboard; Initial indicators of international design capabilities can be found at www.ifm.eng.cam.ac.uk/service/books/#reports. The report on design spend, Company spending on design: exploratory survey of firms 2008, is also available from the same site.

Project partners included the Universities of Nottingham, Strathclyde, Cranfield, Dundee and Loughborough. The work is also supported by the UK Design Council.

Date: 15/04/09
CHINA OFFERS MAJOR OPPORTUNITIES FOR UK COMPANIES ACROSS THE MANUFACTURING VALUE CHAIN ACCORDING TO NEW UNIVERSITY OF CAMBRIDGE STUDY

China is rapidly developing new capabilities across the manufacturing value chain, beyond its established role in mass production, according to a new University of Cambridge report. The study, by researchers at the Institute for Manufacturing’s Centre for International Manufacturing (CIM), identifies many new opportunities for UK companies as a result of China’s continued rapid economic growth.

The report’s publication follows a recent call by Prime Minister Gordon Brown to double Britain’s exports to China over the next 18 months – from £5 billion to £10 billion. Last November the Chinese authorities announced a £400 billion fiscal stimulus which, it is believed, will help create business for British firms.

The Cambridge University report, ‘Understanding China’s manufacturing value chain’, includes case studies in White goods, TFT-LCD and Pharmaceutical sectors. It maintains that opportunities for UK firms exist across the manufacturing value chain in China. These include:

• Forming partnerships with new Chinese centres of expertise in R&D, production and service

• Supporting China’s increasing internationalisation by sharing UK skills in the management of multi-domestic operations and Mergers & Acquisitions

• Building partnerships between UK and Chinese universities, providing opportunities for technology transfer and training

• Engaging with the relatively immature Chinese service sector

While great opportunities are available in cases where particular synergies exist, the report also identifies some risks for UK companies hoping to engage with Chinese organisations. These include intellectual property protection, which the report says needs to be considered carefully. Some foreign multinationals and flagship Chinese firms are developing a range of novel approaches to protect their technologies and brands it reveals.
China’s growing manufacturing capabilities are part of a drive by China to extract greater benefit from its manufacturing sector. Many Chinese firms which started as a regional distributor or contract manufacturer are rapidly moving into adjacent, more value-added positions in the value chain including design or manufacture of their own branded products.

China is making serious investments in many sectors, including aerospace, ship building, steel, IT and telecommunications. Several flagship Chinese companies are providing examples for others to follow and this, coupled with heavy state investment in industry, research and education, means that China is expected to develop its industrial capabilities much faster than other developing economies. Many state-controlled enterprises have grown dramatically with 14 Chinese state industries present in the Fortune 500 list.

Dr Jag Srai, Head of the Centre for International Manufacturing and one of the report’s authors, said: “The report identifies the opportunities for British firms to engage productively with China and the methods used by firms for managing the complexities and risks. It provides some of the mechanisms for ways in which the UK government could achieve its ambition to double exports to China in the next 18 months.”

Date: 17/03/09
In the Winter 2008 edition of The Vitreous Enameller a commitment was made to provide readers with a current list of standards related to vitreous enamel. The BSI technical committee on vitreous enamel coatings, STI/36, is responsible for the following published standards:


- BS 1344-1:1994 - Methods of testing vitreous enamel finishes. Determination of resistance to thermal shock of coatings on articles other than cooking utensils and fabricated sheet steel components.


- BS 1344-22:1994 - Methods of testing vitreous enamel finishes. Determination of resistance to thermal shock of coatings for fabricated sheet steel components such as burners and pan supports for cookers.


- EN 14483-2:2004 - Vitreous and porcelain enamels. Determination of resistance to chemical corrosion. Determination of resistance to chemical corrosion by boiling acids, neutral liquids and/or their vapours.
- EN 14863:2005 - Vitreous and porcelain enamels. Determination of the edge covering of enameled steel plate to be used in heat exchangers.


• EN 15206:2007 - Vitreous and porcelain enamels. Production of specimens for testing enamel on sheet steel, sheet aluminium and cast iron.

• EN 15282:2007 - Vitreous and porcelain enamels. Design of bolted steel tanks for the storage or treatment of water or municipal or industrial effluents and sludges.


• EN ISO 8289:2001 - Vitreous and porcelain enamels. Low voltage test for detecting and locating defects.

• ISO 13804:1999 - Vitreous and porcelain enamels for aluminium. Production of specimens for testing.

• EN ISO 13805:2009 - Vitreous and porcelain enamels for aluminium. Determination of the adhesion of enamels on aluminium under the action of electrolytic solution (spall test).

• ISO 13807:1999 - Vitreous and porcelain enamels. Determination of crack formation temperature in the thermal shock testing of enamels for the chemical industry.

• EN ISO 4528:2009 - Vitreous and porcelain enamel finishes. Selection of test methods for vitreous and porcelain enamelled areas of articles.
There are other standards that contain vitreous enamelling components that are not the responsibility of STI/36 and are looked after by other technical committees:

- BS 4479-8:1990 - Design of articles that are to be coated. Recommendations for vitreous enamel coatings.
- BS 6748:1986 - Specification for limits of metal release from ceramic ware, glassware, glass ceramic ware and vitreous enamel ware.
- BS 6999:1989 - Specification for vitreous-enamelled low-carbon-steel flue pipes, other components and accessories for solid-fuel-burning appliances with a rated output of 45 kW.
- EN 12983-1:2000 - Cookware. Domestic cookware for use on top of a stove, cooker or hob. General requirements.

In addition to the standards listed there are believed to be other standards that have vitreous enamelling components and we are actively working with BSI to identify these. I would be grateful if readers who are using standards not listed in this article that relate to the enamelling industry would contact me with details please. This will assist by providing visibility of documents that require discussion with other committees and BSI.

SAQLAIN ALI
Chairman STI/36
IVE Council Member
MOVES TO SIMPLIFY HEALTH AND SAFETY TAKE EFFECT

Moves to make health and safety laws easier to understand and comply with take effect from today (6th April 2009). The Health and Safety Executive (HSE) is making four changes to the regulations it is responsible for:

- Introducing a new, easier to read version of the law poster that employers must display
- Reducing the number of forms that employers must complete
- Simplifying arrangements for the manufacture and storage of explosives
- Aligning chemical hazard information and packaging with new EU regulations

Judith Hackitt, HSE Chair said: “We are committed to making health and safety work better for everyone. The changes we are introducing today will help ensure that we all benefit from simpler and more effective health and safety regulation – whether that is by making the law easier to understand or getting rid of unnecessary form filling. We have saved businesses more than £300 million since we introduced our simplification plan in 2005 and are continually looking for ways to improve.” Today’s changes are part of an ongoing drive by HSE to reduce unnecessary bureaucracy and make health and safety regulation simpler and more effective.

The biggest of the changes is the introduction of new version of its health and safety law poster and leaflet which will provide clearer information for workers about their right to work in places where their health and safety is properly protected. The posters are a fixture of every workplace in Britain – employers have a legal duty to display the poster in a prominent position or provide each worker with a copy of the leaflet outlining health and safety laws. The new
easy-to-read poster and pocket cards focuses on employees and sets out in simple terms what employers and workers must do, including when there is a problem. HSE is giving businesses five years to switch to the new leaflets and posters – they must be replaced by no later than 5 April 2014. Any employers who choose to keep the old poster after 6 April 2009 must make sure it is legible and keep the addresses of the enforcing authority and the employment medical advisory service up to date.

The abolition of premises registration means that HSE has further reduced the number of health and safety forms that employers in Great Britain have to fill out. Previously most employers were required to notify HSE or the relevant local authority of their premises. The changes mean that: Factory employers no longer have to complete form F9 to notify HSE. Office and shop employers no longer have to complete the OSR1 form and notify their local authority. HSE and local authorities collect information on businesses to help target their work on the greatest risks. Both are looking to improve the way they use and collect business data, including sharing information.

Manufacture and storage of explosives

Changes to the regulations governing the manufacture and storages of explosives also take effect today after a 12 week consultation. The amendments to explosives regulations will reduce paperwork for the police and holders of explosives certificates, which will now be valid for up to five years. In addition, the regulations remove 224 sets of redundant local mine regulations as part of HSE’s continuing mission to simplify, clarify and modernise the law.

A new version of the Chemicals Hazard Information for Supply (CHIP) Regulations has been produced to align CHIP with the new European Regulation on the classification, labelling and packaging of substances and mixtures (‘CLP’ Regulation), which was introduced in January this year. The main changes are to allow suppliers to comply with the Classification, Labelling and Packaging (CLP) Regulation as an alternative to CHIP before the CLP Regulation become mandatory on 1st December 2010 for substances and 1st June 2015 for mixtures, and to provide powers for inspectors to enforce the CLP Regulation as well as CHIP.

Date: 06/04/2009
NEW STRATEGY TO BE LAUNCHED 3 JUNE 2009

The Health and Safety Executive (HSE) will launch its new strategy Be Part of the Solution (Wednesday 3 June 2009). The Secretary of State for Work and Pensions, Rt. Hon James Purnell will give the keynote address. Mr Purnell will be joined by Judith Hackitt CBE, Chair of HSE; Brendan Barber, General Secretary of the Trades Union Congress (TUC); Gilbert Toppin, CEO of manufacturers’ organisation Engineers Employers’ Federation (EEF), and Councillor Sir Steve Bullock, Chairman of the Local Government Association (LGA) Human Resources Panel (and Mayor of Lewisham). There will be an opportunity for questions to the panel. The strategy will explain that for Great Britain’s health and safety record to improve, everyone in the workforce must act together to minimise risks while maintaining business competitiveness. In particular, business leaders will need to ensure that in difficult economic times corners are not cut, resulting in death and serious injuries to workers. HSE’s new strategy will be launched at a press conference on 3 June 2009 at 10am at Westminster Central Hall - Storey’s Gate Westminster, London, SW1H 9NH. HSE is also undertaking research into attitudes towards workplace safety and people’s perceptions of risk. The results are expected to be surprising and will be publicised ahead of the launch of the new strategy.

Date: 13/05/2009

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I. Introduction

The purpose of this paper is to establish a review of various 2C/1F systems, which all contribute to an environmentally favourable application system along with energy savings, increased production, capacity and efficiency.
In the industrialized countries there is an increasing demand for enamel application systems that will reduce ongoing environmental issues. Addressing these concerns will help to bring pollution under control and possibly, to be brought in the future to a standstill. To realize the goal of halting pollution, more and more the principle of “the one who pollutes should pay” will apply. Organizations will be forced to take more stringent, compliant measures.

The driving forces not only concentrate on the environment, but also on the surface quality, economic use of enamel and automatic application flexibility, along with the use of low carbon steel with 0.03 - 0.08% C instead of the more expensive decarburised steel quality with 0.003 - 0.008% C.

A positive contribution to the environment and cost saving can be achieved by:

a. The known process of pre-treatment of the sheet steel by degreasing and rinsing rather than the acid pickling and the nickel treatment

b. Increased enamel material transfer efficiency by utilizing spraying systems with high material transfer efficiency

c. Introduction of low fluorine and fluorine free enamels

d. The re-use of recovered enamel as much as possible

e. Spray booths concept designed as closed systems. The air is cleaned from overspray material and carried back into the working environment by passing through a dry filter

f. The re-use of water by using a waste water cleaning and water recycling system.

II. REVIEW OF THE 2 C/1F ENAMELLING SYSTEMS

The following 2C/1F systems are in use today:

Comparison between the 3 processes:

A) 2C/1F - Powder/Powder
B) 2C/1F - Wet/Powder
C) 2C/1F - Wet/Wet

In principle, these three systems are based on so-called liberty ground coat enamel combinations and therefore suitable on sheet steel, which is just degreased and not acid pickled.
The application technology is based on the following systems:

**a. Powder-Powder**
The powder ground coat and the powder cover coat enamel are applied on top of each other by electrostatic powder application. No drying is needed. The coating is then fired simultaneously. This process was introduced in the USA for one side application and in Spain in 1979 at the company Fagor.

**b. Wet-Powder**
The thin ground coat is applied in the wet system by means of electrostatic or robot spraying and then completely dried. After a very short drying process with infra-red drier the powder cover coat enamel is applied by electrostatic application and then fired.

After the introduction and installation of the first 2C/1F wet/dry system in France in 1987, it still took some time before this process was introduced in other countries. During the following years various manufactures started to use this method for their product enamelling. In 1991 Electrolux Sweden and a second company in France moved to the 2C/1F wet/dry system.

In Italy the firm, Gasfire switched in 1992 from dry/dry to wet/dry (for ranges) and the firm, Indesit (for ranges) started to implement wet/dry in 1992 as well.

Due to the very positive results in Sweden, the Electrolux, the firms Voss in Denmark (for ranges) and Soreman in France (for ranges) both started in 1993 with the wet/dry system.

In 1996 the Italian cooker producers Smalteria, Technogas and Whirlpool also made the move towards the wet/dry system.

Three companies were added to the list in 1997: Gunkol-Teba in Izmir (Turkey), VZUG in Switzerland and Moravia in the Czech Republic.

In 1998 the fourth Electrolux plant followed in Norway.

For 1999 there are two companies on the list: Elekthermax in Hungary and Grepa in Norway.

**c. Wet-Wet**
The thin wet ground coat is applied by means of electrostatic application or dipping (also possibly by electrophoresis).
As no drying is required after this process, the cover coat is applied wet by electrostatic means. After complete drying the enamel layers are fired together.

Some examples of companies where we installed the 2C/1F in wet/wet: in Argentina at Orbis Mertig, in Poland at Fagor Mastercook and Whirlpool (PL)

III. THE STEEL QUALITY AND THE STEEL PRE-TREATMENT

- Although frequently low carbon steel is also used in the application of the powder-powder system a decarburized steel quality is recommended, in particular when the steel is coated on two sides.

- Until now for the wet-powder system (de-greased) decarburized steel was used. Recently acceptable results (one side application) have been reported in using normal steel quality.

- With the 2 C/1 F wet-wet application system good results have been obtained on low carbon steel.

Generally speaking, we can say that the requirements of the customer in relation to the surface aspect might contribute to the choice of the steel quality.

As far as the pre-treatment of the steel is concerned the following points should be taken into consideration:

- The sheet steel should be well de-greased to prevent undesired gas reactions during the firing cycle

- The acid pickling of the steel is not necessary, because in the three mentioned 2C/1F systems a liberty ground coat enamel combination is applied.

- Pickling should therefore be only used when corrosion remains on the steel surface.

IV. THE VARIOUS ENAMEL COMBINATIONS FOR THE 2C/1F SYSTEM

A. The ground coat

The purposes are:

- to achieve a good enamel adherence by using sheet steel, which is only de-greased
to get a faster out gassing from the ground coat before the cover coat is closed

to avoid black spots where we recommend to use a lower softening temperature and higher surface tension

B. The coating thickness of the ground coat enamel

In principle the ground coat layer has to be thin but thick enough to allow various repair and firing cycles.

- a thicker ground coat layer means more gas bubbles, which can pose the problem of so-called pinholes in the cover coat enamel.

- a thick powder ground coat enamel may lead to more heavy gas reactions due to organic mill additions to the powder enamel.

A wet ground coat requires:

Slip parameters for wet ground are:

- milling fineness: 2-5 / 16,900 mesh
- specific weight: 1.45 - 1.60 g/ccm
- thickness: 40-80 microns

For the 2C/1F process a very thin layer on all surface areas is always required. To assure a thin ground thickness (depends on the frit suppliers who have different requirements between 40 - 80 microns) a fully automatically applied coating is needed. The application system for both ground at wet/powder and wet/wet is the same.

C. The cover coat enamels

It is recommended to choose a cover coat enamel which remains “open” on the surface during the firing cycle and fuses at a later time.

In this way, bubbles, which have possibly already risen from the ground coat, can escape. In practice, this means using cover coat enamels with a higher softening temperature.
Slip parameters for wet cover coat are:

- milling fineness: 0.5 – 1.5 /3.600 mesh  
- specific weight: 1.70 – 1.72 g/ccm  
- thickness: 120 - 140 microns

V. FIRING CONDITIONS FOR 2 C/1F 1 FIRE SYSTEM

Generally speaking there are no special firing conditions needed compared to 1C/1F or 2C/2F. Except for powder where the air curtains may have to be adjusted.

VI. GAS REACTIONS AND ENAMEL FAULTS

The most frequent faults happening during the firing of ground and cover coat are black spots and pinholes which have various origins.

Pinholes rise up through the cover coat according the viscosity degree of enamel.

Black spots which are visible in the cover coat result most of the time from gas bubbles deep in the ground coat. The ground coat enters into the bubbles and rises to the cover coat surface.
Typical defects in the cover coat due to gas reactions

Ground + Cover Coat
## VII ADVANTAGES AND DISADVANTAGES OF THE VARIOUS 2C/1F PROCESSES

<table>
<thead>
<tr>
<th>POWDER / POWDER</th>
<th>WET / POWDER</th>
<th>WET / WET</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Smiley Face]</td>
<td>![Sad Face]</td>
<td>![Smiley Face]</td>
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<td>![Smiley Face]</td>
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<td>![Sad Face]</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large production of flat parts</td>
<td>Difficult with complex part design</td>
<td>Limited choice of colours</td>
<td>Air conditioning</td>
</tr>
<tr>
<td>Clean system</td>
<td>Limited choice of colours</td>
<td>Air conditioning</td>
<td>Constant recycling of big quantity of powder</td>
</tr>
<tr>
<td>High degree of automation</td>
<td>Air conditioning</td>
<td>High abrasion of spraying nozzles</td>
<td>High investment costs</td>
</tr>
<tr>
<td>No milling</td>
<td>High degree of automation</td>
<td>Coating thickness up to 80 microns</td>
<td>All colours possible except with cadmium</td>
</tr>
<tr>
<td>No drying</td>
<td>High degree of automation</td>
<td>Coating thickness up to 80 microns</td>
<td>Air conditioning</td>
</tr>
<tr>
<td>Possible smooth surface</td>
<td>High degree of automation</td>
<td>Coating thickness up to 80 microns</td>
<td>Air conditioning</td>
</tr>
<tr>
<td></td>
<td>High abrasion of spraying nozzles</td>
<td>Coating thickness up to 80 microns</td>
<td>Air conditioning</td>
</tr>
<tr>
<td></td>
<td>High investment costs</td>
<td>Coating thickness up to 80 microns</td>
<td>Air conditioning</td>
</tr>
</tbody>
</table>

- Waste water recycling
- Less material efficiency
- Reworks 5-10% higher than P/P or W/P
- Lower investment costs
VIII THE 2C/1F SYSTEM COMPARED TO THE DIRECT-ON WHITE ENAMELLING SYSTEM

A major advantage of the 2 C/1F system is the possibility of replacing the direct-on white enamelling.

Comparison between DWE and Liberty Coat
THE VITREOUS ENAMELLER

The direct-on enamelling was introduced in the early sixties and presented extraordinary advantages to the traditional 2C/2F enamelling system.

The advantages, of course, were that titanium enamel could be applied directly on decarburized steel with a thin nickel layer, just one enamel layer and one firing.

A disadvantage of the very complicated steel pre-treatment (intensive acid pickling and the nickel treatment) were less important than the big advantages like energy saving, enamel savings and the increase in the production capacity.

However, today the expenses for cleaning the waste water are a burden on the budget (pretreatment baths). It can therefore be said that the trend is to invest into the 2C/1F application system instead of the direct-on white enamelling.

This choice also seems to be justified from a technical point of view, certainly with regard to the results obtained today.

Finally, it can be said that when applying a 2C/1F system the steel pre-treatment can be integrated into the enamel application process, leading to less handling of the item to be enamelled. The complicated charging and discharging of the pre-treatment installation is therefore something belonging to the past.

In new installations, passivation can be eliminated as the parts go to the pre-treatment, through the drier and directly to the various application systems.

IX. EQUIPMENT

There is no doubt that the application of enamel on steel in 2C/1F wet/powder or wet/wet has an excellent cost performance ratio. Economics calculation gave that for 50% good results, it was possible to reduce the costs of 25% depending on the conditions of production.

It is nevertheless the prime necessity of the enameller to keep and control strictly the production parameters such as steel quality, pre-treatment, choice of enamel and the choice of the whole plant equipment.

The efficiency of the application process also depends on adequate:
- **pre-treatment systems** by dipping or spraying keeping in one’s mind the ecological aspect of the production

- **spray booths** with low pressure spraying systems allowing a very high efficiency of the overspray recovery inside the spray booth area

*Wet application:*
- **Dry filter technique** collecting the finest enamel particles. A very ecological filtration allowing to resend the filtered air into the enamelling shop.
- **Hanger systems.** A customer specific hanging system creates the highest efficiency of application. Designed with components for single and back to back double hanging concepts, the hangers are flexible for positioning and for hanging parts of different sizes.
- Dryer and furnace
X. CONCLUSION

Improved quality at reduced running costs with less material waste, reliable equipment, latest technology, fully automatic production, low cost maintenance allowing investment savings, are the major factors in choosing and installing the new technology. This is the result of practical experience and customer related research.

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Report from Smalto porcellanato 09/12 2006

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INFLUENCE OF Ag ELEMENT DIFFUSION ON THE ANTIBACTERIAL FUNCTION OF ENAMEL SURFACE

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* College of Materials Science and Engineering, Dong Hua University, Shanghai, China

ABSTRACT

Enamel with excellent antibacterial function can be made by Ag element diffusion at the enamel surface. With the help of SEM and EPMA, the microstructure and Ag element concentration of enamel surfaces after Ag element diffusion were studied, and the influence of Ag element diffusion on the antibacterial function of enamel surfaces was investigated. The results show that Ag concentration in the enamel surface is the main contribution to the antibacterial effect, Ag element diffusion does not damage the surface structure of enamels at the required time and temperature, and the enamel surface still has the excellent acid resistance after the Ag element diffusion.

1. INTRODUCTION

Risk of epidemic diseases pushes scientist to create new products for healthier living environments. A lot of research work has been done on materials with antibacterial performance [1-5].

Enamels are often used in boilers and pipes of water supplies. Although the water that is fed into the drinking water supply network is not generally contaminated with any harmful microorganisms, an increasing number of organisms can occur as a result of water remaining in the pipes and boilers over a longer period of time. The enamels, which are used in hot water boilers, bathtubs, shower basins, architectural panel etc., should not have only excellent chemical stability, but also the antibacterial function [4-7].
The antibacterial enamels, which have been studied, are mainly made by mill addition of compounds with Ag⁺ ion. The disadvantage of these antibacterial enamels is that the antibacterial activity could be influenced by the enamelling firing technology \cite{4,7}. Besides, the chemical stability of enamels is decreased by the mill addition of compounds with Ag⁺ ion. In order to increase the chemical stability of enamels, the enamel should be fired a little longer, which will decrease the enamel’s antibacterial activity \cite{4,6,7}.

In this research work, antibacterial enamels have been made through Ag element diffusion and the influence on antibacterial function of the enamel surface was studied. With the help of SEM and EPMA, the microstructure and silver element concentration of the enamel surface before and after Ag element diffusion were investigated.

2. EXPERIMENT

2.1 Enamel specimen preparation

Enamels which are used for pipes and boilers were selected as the basic testing specimen. The chemical composition range of the enamel frits is shown on the table 1.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>SiO₂+TiO₂+ZrO₂</th>
<th>B₂O₃+Al₂O₃</th>
<th>MgO+CaO+SrO</th>
<th>Na₂O+K₂O</th>
<th>CoO+NiO+MnO₂</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percentage</td>
<td>60–75</td>
<td>5–15</td>
<td>5–10</td>
<td>15–20</td>
<td>1–5</td>
<td>1–5</td>
</tr>
</tbody>
</table>

The enamel frit was manufactured in accordance with ordinary manufacturing technology of enamel frits. After melting, the enamel frit was mixed with suspension agent, electrolytes and water. The mixture proportion is shown on table 2. The mixture was milled into slip and passed through 140 sieve mesh. Steel sheets (size: 100x100x1.0mm), which were treated to remove oil and rust from the iron surface, were sprayed with the enamel slip for the enamel application. After spraying, the enamel specimens were dried and fired. The enamel drying and firing temperature were 100±5°C and 860±5°C. The enamel firing time was 150±5 seconds.
2.2 Ag element diffusion test of the enamel surface

There are three methods for Ag element diffusion of the enamel surface, metallic colloid coating method, metallic salt melting method and metallic salt vapor method\[^8\text{-}10\]. Since colloid coating technology is easy and practicable for Ag element diffusion of enamel surface, the colloid coating method was selected as the diffusion method for testing. The chemical composition of the metallic colloid coating is shown on table 3.

### Table 2: The mixture proportion of slips

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Enamel frit</th>
<th>Clay</th>
<th>Borax</th>
<th>Sodium Nitrite</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percentage</td>
<td>100</td>
<td>4.5–6.0</td>
<td>0.1–0.3</td>
<td>0.1–0.2</td>
<td>45–50</td>
</tr>
</tbody>
</table>

### Table 3: The chemical composition of the colloid coating

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>AgNO(_3)</th>
<th>ZnO</th>
<th>Clay</th>
<th>Glue</th>
<th>Glycerin</th>
<th>H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percentage</td>
<td>100</td>
<td>10–15</td>
<td>10–30</td>
<td>5–10</td>
<td>10–20</td>
<td>20–30</td>
</tr>
</tbody>
</table>

The raw materials, according to table 3 chemical composition of the colloid coating, are mixed, ground, passed the 200 meshes sieve and become the homogenous colloid. The enamel surface is coated with the colloid by brush. The colloid coating thickness is 0.1–0.3 mm. After brushing, the enamel specimen is dried and baked for Ag element diffusion. The drying and baking temperature is 100±5°C and 450±5°C. The enamel baking time is 5–40 min. After baking, the enamel should be dipped into hydrochloric acid, and then, washed with de-ionised water for three times in order to remove the residue of coating on the enamel surface. Then, the enamel should be dried completely and the enamel specimens with Ag element diffusion have been made.

2.3 Enamel tests

2.3.1 Enamel adherence strength test

In accordance with EN10209, the Europe Standard of enamel adherence strength\[^11\], the enameling specimens with Ag element diffusion are tested by the steel ball falling impact test. The adherence strength is judged according to relics of enamel on the destroyed surface after the impact. The enamel adherence strength is graded into 1\(^{\text{st}}\), 2\(^{\text{nd}}\), 3\(^{\text{rd}}\), 4\(^{\text{th}}\), 5\(^{\text{th}}\) grade. If most of the enamel layer is removed from steel sheet and the enamel appears silvery bright after the impact, the adherence strength is poor and 5\(^{\text{th}}\) grade. If most of enamel layer remain on steel sheet and enamel appear black color, the adherence strength is excellent and 1\(^{\text{st}}\) grade.
2.3.2 Enamel acid resistance test

In accordance with ISO 2722, the international standard for acid resistance, the acid resistance of the enamel surfaces with Ag element diffusion was tested. The acid resistance grades for enamels can be classified into 1st grade, 2nd grade and 3rd grade. 1st grade is the best one and 3rd grade does not meet the quality demand of the standard.

2.3.3 Enamel anti-bacterial tests

There are three methods commonly used to investigate the antibacterial function of materials[2-4], Halo test, contact film test and shake flask test. Contact film test is the more accurate method for the coating surface. For this reason, it was applied to investigate the antibacterial performance of the enamel surface.

The enamel specimens were sterilized at 200°C for 2 hours. E-coli colonies are cultivated in nutrient broth at 37°C for 24 hours in shaking incubator. Formed colonies are diluted by dilution solution. Diluted E-coli bacteria solution is dropped to the bottom of the Petri dishes and the enamel specimen surfaces are faced down into them. It is assured that a tiny layer of bacteria with diluted solution has been in contact with the enamel specimen surface. Then, the samples are left in incubators at 25°C and 37°C for 24 hours. After incubation period, the samples are removed from the Petri dishes and the remaining solution beneath the samples is cultivated to supplemented medium in different Petri dishes. Then, the Petri dishes are set in incubator and finally bacteria growth is observed at various time intervals.

2.4 Microstructure and element distribution analysis on the enamel surface

The enameling specimens surfaces with Ag element diffusion are washed with de-ionised water and dried completely, and then, are coated with carbon film. The microstructures of the enamel surfaces are analyzed by scanning electron microscope (JSW-5600LV, Japan). The silver element concentrations of the enamel surfaces are investigated by electron microprobe (EPMA-8705QH, Japan).
3. RESULTS AND DISCUSSION

3.1 Relationship between the enamel adherence strength and Ag element diffusion time

The adherence strength of enamel with different Ag element diffusion time is tested according to EN10209. The results are shown on table 4. It can be seen from table 4 that the enamel adherence strength has not been reduced after different period of Ag element diffusion at 450°C. Therefore, it indicates that baking at 450°C within 40 min. will not spoil the enamel adherence strength.

<table>
<thead>
<tr>
<th>Diffusion time (min.)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enamel adherence strength</td>
<td>1st grade</td>
<td>1st grade</td>
<td>1st grade</td>
<td>1st grade</td>
<td>1st grade</td>
<td>1st grade</td>
<td>1st grade</td>
<td>1st grade</td>
<td>1st grade</td>
</tr>
</tbody>
</table>

3.2 Relationship between acid resistance of the enamel surface and Ag element diffusion time

The acid resistance of enamel surface with the different time treatment of Ag element diffusion was tested according to EN10209. The results are shown on fig. 1. It can be seen from fig. 1 that the acid resistance of the enamel surface has not been reduced when the Ag element diffusion time is less than and/or equal to 30 min. at 450°C. After the Ag element diffusion time is over 35 min, the acid resistance of the enamel surface will be decreased gradually. When the Ag element diffusion time is over 45 min, the acid resistance of the enamel surface is decreased further and does not meet the quality demand. Therefore, there is one period of Ag element diffusion for not deteriorating the acid resistance stability of the enamel surface.

![Fig. 1: Relationship between acid resistance of the enamel surface and Ag element diffusion time](image-url)
3.3 Relationship between Ag element diffusion and the antibacterial function

The reduction ratio on the growth rate of bacteria shows the antibacterial function. E-coli bacteria have been used for the antibacterial function test. Coli form unit (CFU) and colony numbers on the Petri dishes are counted and the following formula are used for the antibacterial function

$$F = \frac{(Co - C)}{Co} \times 100\%$$

F - Antibacterial function
Co - Cell number before the antibacterial testing
C - Cell number after the antibacterial testing

Results of the antibacterial function test of the specimen are shown on fig. 2. Values on fig. 2 are the average of five specimens. Fig. 2 shows the relationship between the enamel surface Ag element diffusion time, antibacterial testing time and the antibacterial function. It can be seen from fig. 2 that the enamel surface without Ag element diffusion has almost no antibacterial function. It can be found from fig. 2 that the enamel surfaces with Ag element diffusion over 15 min. have good antibacterial function. After the 24 hours testing, E-coli has disappeared completely.

It can also be discovered from fig 2 that the antibacterial function of the enamel surface will increase with the Ag element diffusion time elongating when the diffusion time is below 15 min. After the diffusion time is over 15 min., the antibacterial function of the enamel surface hardly increases. Considering the acid resistance stability and antibacterial function, therefore, there is one optimal period for Ag element diffusion of enamel surface. The optimal period should be from 15min. to 30 min (see fig. 1 and fig. 2).

![Fig. 2: Relationship between the antibacterial function and antibacterial testing time](image-url)
3.4 Microstructure and Ag element distribution of enamel surface with Ag element diffusion

It has been reported\(^{7-10}\) that Ag\(^+\) replaces K\(^+\), Na\(^+\) in the glasses and/or enamel in the ion exchange process during the glasses and/or enamels being immersed in AgNO\(_3\) melting salt. Since the quantity of Ag, which diffuses into the enamel, is quite small, it is very difficult to indicate the Ag valence states and the proportion of Ag\(^0\), Ag\(^+\) and Ag\(^{2+}\). It is supposed that the diffusion silver is Ag element in general.

Fig. 3 shows the microstructure of the enamel surfaces with and without Ag element diffusion. It can be seen from fig. 3 that the enamel surface without Ag element diffusion has the smooth and dense microstructure (see fig. 3A). It can be found from fig. 3B and fig. 3C that after 15 and 25 min. Ag element diffusion at 450\(^\circ\)C, there are some small white points in the enamel surface, which should be the result of Ag element diffusion (see fig. 4). It can also be seen from fig. 3B and C that the enamel surface has a smooth and dense microstructure after Ag element diffusion of 15 and 25 min. at 450\(^\circ\)C. The enamel surfaces still have good acid resistant stability (see fig. 1).

Fig. 3A: The enamel surface microstructure without Ag element diffusion
**Fig. 3B:** The enamel surface microstructure after 15 mins Ag element diffusion

**Fig. 3C:** The enamel surface microstructure after 25 mins Ag element diffusion

**Figs. 3:** The microstructure of the enamel surfaces with and without Ag element diffusion.
Fig. 4 shows Ag element weight percent at the enamel surface after the different baking times at 450°C. Values on fig. 4 are the average of five specimens. It can be seen from fig. 4 that Ag element weight percent at the enamel surface increases fast when Ag element diffusion time is below 15 min. After Ag element diffusion time is over 15 min, Ag element weight percent at the enamel surface increases slowly. When Ag element diffusion time is over 30 min., Ag element weight percent at the enamel surface hardly changes. There is Ag element diffusion equilibrium between the colloid coating and to inner enamel layer after the Ag element diffusion time is over 30 min.

![Graph showing relation between Ag element diffusion and diffusion time](image)

**Fig. 4:** Ag element weight percent at the enamel surface after different diffusion times at 450°C

### 3.5 Influence of Ag element diffusion on the antibacterial function of the enamel surface

The uses of silver against diseases and for the preservation of drinking water have a long history. The application of silver has a tradition of about 2500 years. The bactericidal properties of silver are referred to as oligo-dynamic. This term indicated that silver is active even in very low concentration. The inhibition or the destruction of the microorganisms has its cause in the formation of free ions which absorb at the cell surface and react with the SH groups of the enzymes and proteins. As a result, the proteins are destroyed. Through the disturbed enzymatic action, metabolism is impeded, and irreversible damage of the germs may occur [1-3].

With traditional enameling technology, the antibacterial enamels are made by mill addition of Ag-compound [4-7]. The concentration of silver in enamel surface is the same as that in the inner enamel layer. The silver in the inner enamel layer has no contribution to the antibacterial effect. Besides, since the surface tensile effect of melting enamel, silver on the enamel surface will be melted
into the melting enamel during firing\(^{[6-7]}\). Silver concentration on the enamel surface will be decreased and the antibacterial activity will also be impaired\(^{[4-6]}\).

Through Ag element diffusion, silver concentration on the enamel surface is increased greatly (see fig. 4), specially when the diffusion time is over 15 min. The higher concentration of silver on the enamel surface enhances the antibacterial function (see fig. 2). Since Ag element mainly exchange with Na\(^+\), K\(^+\) ion at the enamel surface\(^{[6-8]}\), it does not damage the surface structure of enamels (see fig. 3) when the diffusion time of Ag is below 30 min. The enamel surface still has the excellent acid resistance after Ag element diffusion (see fig. 1). The enamels with Ag element diffusion have not only the good acid resistant stability, but also the excellent antibacterial property.

### 4. CONCLUSION

Through the experiments, results and discussion, the conclusion is as follow:

1. The enamel with the excellent antibacterial function can be made by Ag element diffusion at the enamel surface.

2. Ag element diffusion of the enamel surface at the required time and temperature does not damage the surface structure of enamels, and the enamel surface still has the excellent acid resistance after Ag element diffusion.
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[11]. EN10209 Determine of the adherence

CORRESPONDENCE

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1. ABSTRACT

It turned out to be possible to develop foam enamels from foaming enamel slurries using inorganic substances which release gases at the typical annealing temperature of enamels. To get a general idea of potential foaming agents able to produce gases, a catalogue was provided of all relevant compounds. In doing so, toxic, radioactive or extremely expensive materials were excluded. In general high temperature resistant carbides, carbonates and inorganic water containing compounds as well as mixtures were suitable as foaming agents for the preparation of foam enamels.

From this catalogue some substances suitable from technical aspects of glass and enamel production were chosen and experiments were performed to foam three slurries. Substrates, ways of preparation, annealing temperatures and firing times as well as the water contents of the slurries were varied. Slurry compositions were modified as well as the process engineering (preparation, layer thickness of the coat, drying time, baking regime) had to be adapted to the special needs of these enamels as thick layers. Thus a special cooling procedure had to be applied dependent on the thickness of the coatings. The common additives of conventional enamels, e.g. quartz and zircon, degrading generally the porosity of enamels, were omitted. The water content was chosen as low as possible. In addition, the viscosity of the slurry was adjusted with potash ($\text{K}_2\text{CO}_3$) to obtain a paste-like coating on the steel plates.
Pore volumes of about 87 Vol.% resulted with an addition of 2.5% SiC to a ground coat, in contrast to a pore volume of only 78 Vol.% with 2.5% SiC added to a cover coat. The origin of the low porosity of the cover coat enamel and of the lower maximum content of foaming agents to be mixed is due to the chemical composition of the cover coat enamels. These cover coats use to melt earlier forming a plane surface.

It has been proved that the melt viscosity of the enamel and the temperature-viscosity-behaviour of the foaming agent, which depends on the chemical composition, have a strong influence on the formation of foamed enamels.

The best foaming agent for conventional enamels is SiC as an additive to the slurry with contents of 2.5 - 5%. It increases the viscosity of the enamels and therefore the stability of the foam.

Other foaming agents, e.g. potash and limestone, decrease the viscosity of the enamel melts making them less suitable at usual annealing temperatures. Alkali and alkaline earth carbonates form gases at the annealing temperature of the enamels. This probably makes them applicable for slurries that melt at higher annealing temperatures, e.g. for enamels for the production of chemical apparatuses. Soda (Na₂CO₃) is unsuitable as a foaming agent, for it results in a “short glass” with a narrow temperature range of melting.

Special procedures to investigate the chemical and the thermal resistance of foam enamels were developed and modified, respectively.

It was verified that the chemical resistance of foam enamels is similar to that of conventional enamels if appropriate foaming agents and a suitable baking regime were used.

The coefficients of the thermal conductivity specific for the material proved to be suitable, i.e. the U-coefficient (coefficient of the thermal conductivity independent of the layer thickness) of the foamed ground coat was 5.7% of that of the conventional enamel with the same layer thickness.

Thus foam enamels are best qualified to protect other sensible parts in buildings, e.g. in tunnels, tubes and airports. This is due to the non-toxic, inflammable properties of enamels.
2. INTRODUCTION AND OBJECTIVES

Since the enamel and steel industries are keen to explore new areas of application, it makes sense to develop alternatives to organic insulating materials for structural engineering. This is due to their higher durability, resistance against fire and humidity as well as the environmental sustainability of enamels[^1]. The required properties (thermal, acoustic, vibrational insulation) can be obtained by thick-layer (10 - 20mm) foamed enamels containing a high percentage of enclosed pores. Therefore the purpose of this study was the development of novel inorganic enamels on steel substrates, with coatings executed as foam enamels like foamed glass. Organic insulating materials and adhesives, on the other hand, are flammable and are able to emit toxic vapours while burning.

The most important property parameter of these new foam coats is its porosity. It should be by 80 - 95 Vol.% of the volume of the coating to ensure a low thermal conductivity and a respective high thermal insulation. Despite this high porosity a sufficient compressive strength and a good adhesion were to be assured. These foam enamels are provided to be used for panels of architecture in the construction industry, where the rear side is executed as a foamy insulating coat and the front side as an aesthetic thin layer of enamel. Further technical applications should be possible in energy, environmental, chemistry, automotive and traffic engineering and for fire protection.

3. LITERATURE OVERVIEW

3.1 Porosity of enamels

One publication has been found only concerning the preparation of foam enamels[^2]. Fig. 1 shows the results obtained using 15% SiC of two grain sizes added to common enamel slurries. However, this foam enamels contained pores up to 10mm, which make the surface of those enamels unsuitably uneven when fired at the common baking temperatures of enamels[^2].
Pores in unfoamed enamels display a defined distribution of bubbles, being desired for compensation of the different thermal expansion coefficients and as space for storage of the gases (\(\text{H}_2\), \(\text{H}_2\text{O}\), \(\text{CO}_2\)), emitted during the production of the enamels. The addition of quartz (\(\text{SiO}_2\)) and zircon (\(\text{SiO}_2\ \text{ZrO}_2\)) to the mill reduces this porosity of enamels to \(\approx 15\ \text{Vol.}\%\) \([3][4][5]\).

### 3.2 Foaming agents to manufacture foam enamels

To find suitable foaming agents for the preparation of foam enamels, potential foaming compounds were inspected. Radioactive or extremely expensive substances were excluded. Well-known fining agents for glass production (e.g. sulfates, nitrates, sulfides) were not considered since they emit toxic gases at high temperatures. On the other hand compounds like hydrates (borates, aluminates, silicates, to some extent also phosphates), carbonates, carbides and manganese dioxide seemed to be potential foaming agents, particularly also because cations like \(\text{Si}^{4+}\), \(\text{Na}^+\), \(\text{K}^+\), \(\text{Ca}^{2+}\) are suitable compounds both in glasses and enamels\(^6\).
4. PREPARATION OF FOAM GLASS AND FOAM ENAMELS

From these groups of compounds substances like SiC, Na$_2$CO$_3$, K$_2$CO$_3$ and CaCO$_3$ were chosen for the experiments. The criteria of choice were availability, prize and especially the behaviour as raw material with respect to viscosity and chemical resistance.

The structure of the experiments is illustrated in Fig. 2. According to this we tested the possibility to prepare foam enamels as well as foam glass (for comparison) and the addition of porous aggregates. For preliminary tests we used dry enamel powder mixed with foaming agents in a muffle furnace. The final tests we carried out with steel sheets and enamel slurries mixed with the powders of the foaming agents in chamber kilns.

Further the temperature regime of the blowing process was examined in a tube furnace heated at a rate of 20K/min. After foaming properties like adhesion, chemical stability and thermal conductivity were checked. All these tests had to be adjusted appropriately to the needs of the foam enamels with regard to their high porosities.

![Fig. 2 Structure of the experiments](image)
A usual enamel firing regime with 2 firing times (2 and 4 min) and 2 firing temperatures (800 and 820°C) was used. Due to the high thicknesses of the raw coatings (4mm) and of the foamed enamel coatings (up to 20mm) a cooling process like that for a standard glass had to be introduced.

As samples two ground coats (1 Premix of commercial recipe, 1 with a modified recipe) and 1 cover coat with a modified recipe were applied. The modifications of the recipes of the slurries were:

- elimination of any crystalline addition to the mill (quartz and zircon)
- decrease of the water content (47 ⇒ 42%) of the slurry
- increase of the content of the set-up agent potash of 10%

in order to get a stable layer while coating. The chemical compositions of the samples used is shown in Fig. 3, demonstrating that the network forming components being high in the cover coats like in foam glass but are relatively low in the ground coat. In contrast the contents of the alkali oxides and the intermediate oxides are relatively high in the ground coats. As shown later this is important for the formation of a melt of high viscosity and therefore also for the formation of a stable foam.

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**Fig. 3** Chemical compositions of enamel and foam glass
5. RESULTS

5.1 Experiments to prepare foam glass and foam enamel

5.1.1 Porosity of foam glass and foam enamels

5.1.1.1 Foaming experiments with dry enamel powder

By means of preliminary tests with dry enamel powder (Fig. 4) foam enamels were made from Premix with 10% SiC. It will be shown later that using the modified enamel recipes (slurries) less foaming agent is required. These preliminary tests proved that organic materials like different kinds of wood, sugar, flour or cream of tartar were not suitable due to their low temperatures of firing. Inorganic agents like gypsum, CaSO₄, borax or MgCO₃ reduced the viscosity of the enamels, being unable to result in a stable foam, had to be eliminated. Thus only potash and SiC turned out to be suitable foaming agents in dry enamel powders with a concentration of 10%.

Water insoluble SiC with a melting point of 2700°C is being corroded by the enamel melt while the carbon is oxidised to CO and CO₂ [⁶]. The silicon is integrated into the matrix of the enamel increasing the viscosity. The water soluble potash (m.p. 891°C) also reacts and pyrolises in the melting range of the enamel (K₂CO₃ → K₂O + CO₂↑) [⁶]. The formed K₂O is introduced into the enamel matrix being there the decisive component of “long glasses”, extending the melting range of the enamels where the highly viscous melt is able to keep the CO/CO₂ gases in the foam.

As will be shown later, the mechanism of potash introduction is different in dry enamel powder to that in hydrous slurries. This is due to the solubility of potash in the hydrous slurry caused by the formation of hydrogen carbonate bonds.

Fig. 4 shows an image of a foam enamel prepared from Premix and SiC. There the filling degree of the enamel powder is marked, thus the increase of the volume caused by the foaming is recognisable.
5.1.1.2 Foaming experiments with glass

In comparison to foam enamel experiments with recycling glass were carried out, using SiC as a foaming agent. It could be shown that there is an optimized concentration of foaming agent (2.5 - 5%). Above this range of concentration too many bubbles were formed, which coalesced with other bubbles becoming big ones. These bubbles are able to ascend to the surface, then leave the sample (degasification) and decrease its volume. This is the reason why the previous study\(^\text{[2]}\), where too much foaming agent was applied, failed. Fig. 5 shows the dependence of the increase of the volume caused by the addition of SiC. Thus concentrations of 2.5 - 5% SiC were used for the final tests, elucidating the independence of temperature, concentration of the agent, kind of agent selected and enamel slurries. In a test Fig. 6 confirms that the microstructure of the foam glass consists of enclosed pores of approximately same size.
Fig. 5 Foaming tests with recycled glass

Fig. 6 Foamed recycled glass with 5% SiC
5.1.1.3 Foaming experiments with enamel slurries

Fig. 7 displays that the optimised amount of 2.5 - 5% SiC does not only hold for foam glass but also for enamels. However, a semi-quantitative inspection shows that besides the high porosity also a smooth surface is important. This is evidenced by the standard deviation of the porosity which is deduced by measuring the coat thickness of the foam enamels. Furthermore it may be seen from fig.7 that in contrast to Premix (commercial recipe) the enamel slurries (modified recipes for ground and cover coats) result in higher porosities and lower standard deviations. Therefore a standard deviation > 1 Vol.% already is an indicator that degassing causes lower porosities and a lower smoothness of the foam enamel surfaces. This is only avoidable by a decrease of the concentration of the foaming agent and/or a lowering of the firing temperature. However, high firing temperatures are inevitably necessary to guarantee a sufficient adhesion between the enamel coating and the steel sheet.

Fig. 7 Ground coats with porosities > 80 Vol%}

Fig. 8 shows the porosities as a function of different agents (B₄C, MnO₂, SiC + CaCO₃, SiC + K₂CO₃, citric acid, baking powder and foam glass) and different enamels (Premix, ground and cover coat with modified recipes). This evidences the efficiency of the foaming agent SiC. Any addition to SiC even decreases the porosity and/or increases the standard deviation i.e. the roughness of the surface. Salts like potash or baking powder which result in high porosities in the dry powder are less efficient (porosities and standard deviations) in the case of foam enamels made from water slurries. These salts are dissolved in water, forming carbonic acid, decomposing already at low temperatures. Agents
containing cations like $\text{B}^{3+}$ or $\text{Mn}^{4+}$, which are important components of enamels, decrease the viscosity of the melt, thus a stable foam formation is impossible (easy degassing).

**Fig. 8** Porosities of different foam enamels

**Fig. 9** Typical foam enamels with high porosities

Fig. 9 exhibits successfully prepared foam enamels made from enamel slurries. Thus it is proved that the best foam enamels can be made using modified enamel slurries with SiC. Due to its easily obtainable smooth surface the cover coat does not show such a high porosity compared to a ground coat.
Advantageous for the formation of foam enamels is that the enamel melt shows a wide range of melting temperature with a high viscosity ("long glass"), with particles of the slurry of approximately the same size\(^7\).

### 5.2 Properties of foam enamels

#### 5.2.1 Chemical resistance

With regard to conventional enamels the testing procedure for the chemical resistance of foam enamels had to be modified since it turned out to be impossible to use plates of foam enamels which are able to close the testing cylinder according to EN 14483. Instead DIN 719 was applied accordingly. Coatings of the foam enamel were removed from the steel substrates,hammered to sizes of 125 – 250\(\mu\)m and cooked in boiling water for 2h. The loss of mass after boiling served as an indicator for the chemical resistance.

An important result was that the chemical resistance of the foam enamels is lying in the same range as that of unfoamed enamels. According to Fig. 10 the resistances seem to be dependent on porosity. The reason for that is that apparently the fraction of pores < 125\(\mu\)m is very high. Thus the real surface is much higher than the calculated one. Future investigations should apply e.g. adsorption methods to determine the porosity in order to obtain the specific surface of the foamenamel powder. However, it has to be borne in mind that while using foam enamels their surfaces have to be as smooth as possible (standard deviation of the porosity < 1 Vol.%). Therefore in reality not the closed pores but only the surface of the foam enamels is of importance for the chemical resistance.

![Fig. 10 Chemical resistance of foam enamels](image)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image}
\caption{Chemical resistance of foam enamels}
\end{figure}
5.2.2 *Thermal conductivity of foam enamels*

The preliminary thermal conductivity of the foam enamels was estimated by a - not yet fully developed - laser method. However, Fig. 11 indicates that the foaming effect considerably decreases the thermal conductivity\(^8\).

![Fig. 11 Thermal conductivities of foam enamels](image)

**6. CONCLUSIONS**

It was proved by this investigation that both a systematic development and preparation of foam enamel is possible, especially if the recipe is modified. Further a very fine grain size of the foaming agent and a very good homogenisation of the raw materials is necessary. Already low concentrations (2.5 - 5\%) of the foaming agent give satisfying performances. A high viscosity of the slurry as well as of the melt is important. Firing temperature and time are nearly independent of the foaming agents. However, both special firing and cooling routines are necessary. The chemical resistance is approximately the same as in the case of unfoamed enamels.
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