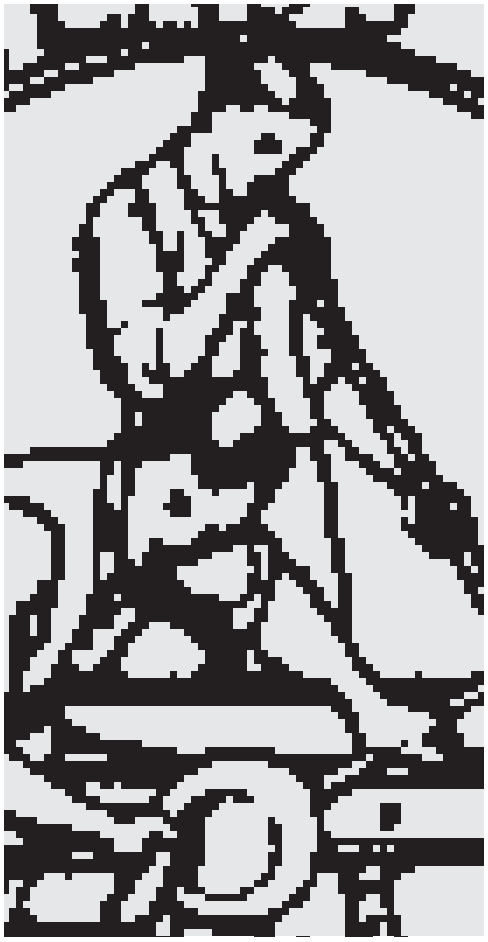

NO. 6 2004

SGT NEWS

Compiled and published by dmg world media (uk) ltd on behalf of the Society of Glass Technology

ALKALIS FOR THE ST HELENS GLASSMAKER THROUGH THE AGES

Alkalis are an essential ingredient in most glasses. St Helens developed into one of the major centres of glassmaking in England and in its heyday produced flat glass, bottles, tableware, insulation and TV screens, using various alkalis to help give the specific properties of the glass produced. At the first meeting of the Society of Glass Technology's North West Section *David Bain* looked at the changes in the alkali industry in St Helens from the early days to the present. The meeting was jointly held with the Contemporary Glass Association at the World of Glass in St Helens.

Glass is everywhere, and there are numerous different types from pure silica glass to ones which do not even contain silica. Each has a different chemical composition and contains a number of different raw materials, but we will concentrate on the 'common' soda–lime–silica glasses and the alkalis that have been used in them.

Why add alkalis to glass in the first place? We can make a pure silica glass, however it has a very high melting point (>2100°C) and is very difficult to work. Alkalis act as a flux for the glass to enable it to melt at lower temperatures. With the 'stabilisers', ie calcium oxide, in the mix the working characteristics of the glasses are determined in the forming processes.

The first mention of glasshouses in the St Helens area of South West Lancashire was in 1696. St Helens continued to be a small glassmaking area until the 1770s when the first cast plate factory in the country was established at Ravenhead. But where did these early glassmakers obtain their alkalis?

Maritime plants grew in the salt marshes by the sea and 'Salsola', 'Chenopodium' and 'Salicarnia' were vaguely referred to as 'kali'. Burning these types of plants produced an ash rich in sodium, which is where we get the name 'soda ash'. These ashes were called 'rochetta' but the purest forms were produced in Spain by burning plants of the goosefoot family, which were grown extensively in Spain, Sicily and Tenerife to make 'barilla'.

How was 'barilla' made? The plants grew as round, thick shrubs and were harvested, roots and all, when the berries were ripe. They were tied together and dried for several days in the sun. A 6-feet deep pit was dug and the plants were placed on a grid over the pit and set alight. The berries melted into an azure-coloured liquid which was allowed to cool and, when set, a blue stone was removed which was scarcely malleable. This was broken down and sold across the developed world; in 1604 the price of barilla was 10 shillings per hundredweight.

Burning other plants such as fern, bracken and beechwood also produced alkaline ashes which were potassium rich and this gave the name 'potash'. European glassmaking was mainly in Germany and Northern France, where the wood from extensive forests was used as fuel in the glasshouse and the ashes became a 'free' source of alkali.

In St Helens there was not such an abundance of woodland so two sources of ashes were used - 'barilla' from Spain and the burning of seaweed 'kelp' in Scotland. The ashes taken from the burning of kelp were less rich in soda – about 10% - than in barilla, which was around 20%.

In the 1770s when the cast plate factory was built at Ravenhead the fuel source was local coal. The glassmakers had a problem in securing adequate supplies of alkaline ashes, as the major users were the soap boilers in London and Liverpool and the saltpetre men. In 1818 it was estimated that the soap boilers consumed 90% of the barilla and 70% of the kelp ashes used in this country.

Old recipes talk about the addition of soap lye and ashes

from the glasswort plant. The other major problem that the St Helens glassmakers had was the economics of the process. There was an import duty placed on the barilla which was fixed sufficiently high to allow kelp ashes to be sold at competitive prices despite their differing soda content. In August 1822, however, this delicate balance was upset when the duty on barilla was reduced from £11 to £5 5s 0d.

This caused major problems in the kelp industry and the associated soap making industry in nearby Liverpool. In the mid-1820s the duty on the sale of salt was removed, which led to the widespread adoption of a new method of making soda from salt. This was invented by Nicholas Leblanc at the beginning of the French revolution and developed commercially in France when the wartime blockade drove up the price of barilla:

$$2NaCl+H_2SO_4=NaSO_4+2HCl$$

$$2NaSO_4+4C+CaCO_3 = Na_2CO_3+CaS+4CO$$

The first factories using the Leblanc process were set up in Liverpool, but following environmental pressures and disagreements with the Liverpool Corporation they moved out of the city. A factory close to the double locks on the Sankey Canal was set up, which had the advantages of an abundant supply of cheap local coal from nearby collieries, and of water either from the canal or Windle Brook. Salt could be delivered direct from Cheshire and limestone, needed in the second part of the process, by canal. St Helens was large enough to house local labour but small enough not to possess any organised form of local government which might restrict the growth of the factory. The town grew to be the centre of the chemical industry with many alkali works being established.

During the 1830s the glassworks of St Helens changed from barilla and kelp to the products of alkali, using the cheaper saltcake from the first stage of the process. At the plate glass works, this substitution took longer to happen as this process required a purer source of alkali, but it was still completed by 1868. Many glass firms also started to make their own saltcake. The Eccleston Crown Glassworks made their own in the 1830s and the Union Plate Glassworks, in an account in 1843, mentions a "salthouse" for "preparing the alkali" and another account describes a "very tall chimney" for dispersing the noxious vapours. These chimneys had to be large as the emissions of the HCl gases and the hydrolysis of the calcium sulphide caused horrendous environmental problems.

Saltcake continued to be used until the early part of the 20th century when it was replaced by soda ash. There were several factors that caused this change:

Glassmakers required much purer raw materials and the saltcake obtained from the Leblanc process was not as pure as the soda ash from that process, nor from the ammonia soda process:

$$2NaCl+CaCO_3=Na_2CO_3+CaCl_2$$

This had first been developed in the early part of the 19th century but was made economically viable by Ernest Solvay in Couillet in Belgium in the 1860s and taken up by Brunner and Mond in Northwich. The economics of the ammonia soda process were only about 70% of that of the Leblanc process. This meant that the majority of the older factories were closed by the early part of the 20th century and the cost of soda ash was lower – it had halved between 1875 and 1905.

Associated products from the Leblanc process included chloride and bleaching powder and in the late 1890s the new invention of the electrolysis of salt was made, which produced caustic soda and chlorine (and bleaching powder) more economically.

These factors led to the closure of all the Leblanc alkali works in the area. Consequently in the first 20 years of the 20th century the replacement of saltcake by soda ash as the major source of alkali in the glass batch in soda lime glasses was complete. However some soda is still obtained from saltcake that is still added as a refining agent.

The development of the soda ash industry was one of the many factors which led to the formation of ICI in 1926, which became the major supplier of soda ash to the glass industry in St Helens.

Soda ash supply for the St Helens glass industry continues to be very competitive with the best synthetic product being available from the local producer. It has also been supplied during the past 30 years from across Europe, including Russia, Turkey and Romania, and possibly China. Soda ash obtained from Trona, the mineral ore found extensively in Wyoming, has been used since its introduction in the late 1970s. It has been postulated that if this ore was anywhere else than in the centre of the US, there would not be any serious synthetic manufacture of soda ash in Europe.

There have been some attempts to use caustic soda in the batch with some major work carried out in the 1960s, and some glasses are made overseas in this way, but there are three factors against its use:

- Health and Safety issues in its handling – in solution it is a corrosive liquid and great care has to be taken in its use. It is normally sold as a liquid as the solid is hygroscopic – the standard concentration is 47% thus the glass batch would probably be difficult to handle.
- Economics – the price of caustic soda used to cycle between $50-500 per tonne every seven years. This cycle has now been broken but there are still large price fluctuations.
- The replacement of some of the soda ash by lithium carbonate has not yet gained any real acceptance, as the ore is not very pure and more expensive than the pure form of soda ash.

As with all manufacturing processes, changes have been made over the years in this industry and it can be expected that further changes are inevitable. It will be interesting in 2104 to look back at this industry and the alkalis used. ■

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SGT NEWS

GLASS: PAST, PRESENT AND FUTURE

The 2005 Annual Meeting of the Society of Glass Technology has moved to September. The meeting will be held in Sheffield and marks the 90th anniversary of the founding of the Department of Glass Technology and the centenary of the University of Sheffield's Charter. From 7-10 September next year there will be events celebrating the contributions made by the Society's founder, W E S Turner, the first Professor of Glass Technology, and his continuing influence.

SESSIONS CELEBRATING THE WORK OF PROF M CABLE AND PROF H SCHAEFFER

A key aim of the meeting is to celebrate the contributions that Professors Cable and Schaeffer made over many years to glass science and technology. Sessions will be devoted to their research interests, presented principally by speakers they have worked with.

INDUSTRIAL AND SCIENTIFIC SESSIONS

Sessions covering the imminent emissions trading scheme, quality and six sigma, melting technologies, as well as the latest developments in glass research in the UK and beyond. The New Researchers Forum on Glass will return with updates by students at various stages in their research.

TURNER MEMORIAL LECTURE

Dr David Whitehouse, director of the Corning Glass Museum and editor of the *Journal of Glass Studies*, will present the Turner Memorial Lecture on Thursday 8 September.

HISTORY AND HERITAGE OF GLASS

The Special Interest Group will hold another in its series of one day meetings on Saturday 10 September, based at the Turner Glass Museum. A historical theme will also be covered by the Turner Memorial Lecture and some of the contributors to the session celebrating Professor Cable.

The Annual Meeting will be based at Halifax Hall of Residence with the Turner Memorial Lecture and the following conference dinner held in the main University complex.

Further details on the conference can be obtained from Christine Brown at the Society. ■

ADVANCES IN GLASS MELTING PRACTICE

Professor Michael Cable has edited and translated a series of books that demonstrates how advances in science, especially chemistry, influenced the development of glass melting practice from the middle of the seventeenth century to almost the middle of the nineteenth, by making available in English the works of authors of those times.

The first, published as *The World's Most Famous Book on Glass Making* in 2001, was Christopher Merrett's *The Art of Glass* (1662), a translation of Antonio Neri's *L'Arte Vetraria* which was first published in Florence in 1612 and reprinted in 1661. It also includes an essay by W E S Turner explaining the importance of Neri/Merrett. In the seventeenth century the classical or alchemical four element theory of matter still governed thinking about chemistry and there was little understanding of glass making.

The second translated the works of Paul Bosc D'Antic, written in France between 1758 and 1780. D'Antic had some experience of glass-making and his writings show a very earnest desire to understand glass melting in terms of the latest scientific ideas, but the ancient four-element theory of matter was still accepted at that time. Despite that, the different chemical identities of a considerable range of useful elements and compounds had by then been recognised, although analytical tools were very few and primitive.

The role of heat in melting or solidification and chemical reactions was still confused by the belief in phlogiston as a chemical substance. However, that belief was only a few years away from collapse as attempts to interpret chemical phenomena by invoking it became ever more tortuous. This is clearly seen in some of D'Antic's writings. Nevertheless he reports some ingenious experiments and penetrating observations.

The third volume contains translations of articles by two authors, Scholz and Kirn, writing in German between 1820 and 1837, which show a great advance. They also provide the most detailed known first-hand accounts of European glass making practices early in the nineteenth century. Both technological and economic factors are discussed at length; between them they give batch compositions and comment on the melting behaviour of 80 different glass compositions.

Given such a considerable body of quantitative data, it is surprising to find that these papers seem to have been totally neglected for more than a century. The last author to indicate knowledge of any of these papers appears to have been Tscheuschner, whose compendium published in 1885 included an atlas with 421 diagrams, mostly borrowed from other publications.

***The Art of Glass: The World's Most Famous Book on Glass Making*. A5 (210 mm x 148 mm), 436 pages, ISBN 0-900682-26-4. Paperback. Fourth print. £17.50 (£15.00 to SGT members + £3.00 postage).**

***Bosc D'Antic on Glass Making: Including essays on the manufacture of faience and the assaying of ores*, published 1758–80. A5 (210 mm x 148 mm), 250 pages, ISBN 0-900682-44-2. Paperback. £25.00 (£20.00 to SGT members).**

***Early Nineteenth Century Glass Technology in Austria and Germany: The works of Professor B Scholz and Factory Superintendent Kirn* 1820–37. A5, 340 pages. ISBN 0-900682-45-0, £25.00 (£20.00 to SGT members).**

Orders can be made through the Society of Glass Technology's website (www.sgt.org).

LOCAL SECTION CONTACTS
For details of forthcoming local section events in your area, contact the following. All SGT members and non-members welcome.

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THE FIFTH INTERNATIONAL CONFERENCE ON BORATE GLASSES, CRYSTALS AND MELTS:

NEW TECHNIQUES AND PRACTICAL APPLICATIONS

The Fifth Borate Conference will be held on 10-14 July 2005 at the University of Trento in Italy. Professor Giuseppe Dalba of the Department of Physics will be the conference chairman. The fifth conference follows the previous meetings held at Alfred in New York, USA (1977), Abingdon in England (1996), Sofia in Bulgaria (1999) and Cedar Rapids in the USA (2002).

The Fifth Borate Conference will focus on new techniques in the study of the structure and properties of these materials, as well as their practical applications.

Topics to be covered will include:

- short and intermediate range order in borate glasses and melts
- EPR, XAFS, XPS, IR, Raman, NMR, and diffraction studies of borates
- new spectroscopic techniques
- structure and physical properties
- novel borate glasses and crystals
- thermodynamics of borate systems
- local thermal properties
- optical properties and materials
- computer simulation and modelling
- industrial applications
- phase separation and inhomogeneities
- superionic systems and ionic conductivity
- biomedical applications, and
- mineralogical crystals.

The conference will provide an opportunity to make oral presentations as well as contribute to a poster session. Special allowances will be taken to ensure time for questions and discussions, as well as to organise round tables on topics of particular interest for the participants. The Conference will conclude with a summary discussion held amongst all the attendees.

Accepted abstracts will be prepared in booklet form and given to the attendees at the conference. Presented papers will be refereed and selected for publication in the proceedings of the conference, which will also include the round table discussions. The journals *Glass Technology* and *Physics and Chemistry of Glasses* have again been chosen to publish the peer reviewed papers.

Located at the crossing of some important thoroughfares between Lake Garda and the Dolomites, Venice and Verona, and Bolzano and Innsbruck, Trento is a Renaissance jewel set in the Alps. Founded by the ancient Romans and today bridging the Italian and central European cultures, Trento maintains a unique Renaissance style in its prestigious monuments. This style was inherited by the most enlightened Prince Bishops, who governed the town for eight centuries and made it the seat of the XIX Ecumenical Council in the Sixteenth century.

The conference will take place at the Panorama Conference Centre, which is located on a rocky spur about 560 metres above sea level. The place is quiet and isolated, but very close to the town centre, which can be reached by car in 10 minutes and cable car in four minutes. The Centre has a large conference room, two small meeting rooms, a hotel and a restaurant.

For further information about the conference, contact the Chairman, Giuseppe Dalba, at the University of Trento, Dipartimento di Fisica, Università di Trento, Via Sommarive 14, 38050 Povo, Trento, Italy. Email: borate@science.unitn.it ■

ELECTRONIC JOURNALS

The refereed papers from *Glass Technology* and *Physics and Chemistry of Glasses* are available over the internet via the Society of Glass Technology website (www.sgt.org). This is a new feature and is available to both members and non-member subscribers of the journals.

The Society is working with Ingenta, the leading host of professional and academic publishers on the web, to provide this service. The issues that can be viewed online are from the 1998 volumes onwards. The 2002 volumes onwards also have links from their references to other online publications and reciprocal links will be built up from other electronic journals. This will provide better services for authors and researchers alike, cross-linking the mass of information available.

Since its launch in May 1998, Ingenta has grown to become a leading web infomediary, empowering the exchange of academic and professional content online. With the acquisition of another major provider, Catchword, Ingenta supplies access to more than 5400 full-text online publications, and over 26,000 publications in total. The company serves a growing global audience of academic and professional publishers, which include more than 10,000 academic, research and corporate libraries and institutions, incorporating 25 million users worldwide. It records around three million monthly user sessions.

The title, authors and abstracts of other journals can be viewed online, and a pay-per-view facility is offered for anyone wanting full access to the publication. Members with more than three years service will have full access to all the available issues. More recent members will have graduated rights to view the volumes: two years for a new member, an additional two for those renewing for the second year, and full rights for subsequent renewals.

The December 2000 issue of *Glass Technology* and the June 2001 issues of *Physics and Chemistry of Glasses* are freely viewable as sample publications.

For further information either view the links from www.sgt.org or www.ingenta.com

JOURNAL OF THE SOCIETY OF GLASS TECHNOLOGY

The *Journal* was published by the Society until 1959 when it was split into parts A and B: *Glass Technology* and *Physics and Chemistry of Glasses*. The 1918 and 1952 volumes of the *Journal* can be viewed from the Society of Glass Technology website (www.sgt.org).

The contents pages of all the volumes from 1917 can be viewed on the SGT website. Copies of papers can be copied to order.

The contents pages of *Glass Technology* and *Physics and Chemistry of Glasses* are also now available to view on the SGT website.

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