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GAS 2018
MURANO
IL PERCORSO DI VETRO
THE GLASS PATH

The Future of Glass Colour

in murano
associazione culturale no profit

GAS GLASS ART™ SOCIETY

The future of glass colour
Round-Table, 19th May 2018
GAS Conference 2018 – The Glass Path
Murano

Participants

Michele Back – Kyoto University
Cristiano Ferro – Effetre glassfactory
prof. Francesco Gonella – Ca' Foscari University
Sandro Hreglich – former researcher for SSV Murano
prof. Antonio Pires de Matos – Universidade NOVA de Lisboa
prof. Carlo Pantano – PennState University
prof. John Parker – Sheffield University
prof. Setsuhisa Tanabe – Kyoto University
Caterina Toso – association InMurano

Participants

Michele Back

Michele Back obtained both his B.Sc and M.Sc in Materials Science and he completed his Ph.D. degree cum laude in Chemical Sciences at Ca' Foscari University of Venice, Italy (January 2017) in the field of photonic materials. Currently, he is Post-doc (JSPS Fellow) at the Photonic Materials Laboratory of Kyoto University (Japan) under the supervision of Professor Setsuhisa Tanabe.

His research interests include the design of bulk and nanoscale inorganic materials with advanced optical properties for applications in the fields of bioimaging, telecommunication and phosphors. At present, his research is focused on the synthesis and characterization of bismuth-based luminescent materials and optical thermometers. He is author of 20 peer-reviewed publications and 2 international patents.

Cristiano Ferro

Cristiano Ferro is part of an ancient Murano glass-making family. Cristiano has always been involved in the family business and he is now the managing director of Effetre Murano srl.

He is president of Confindustria Venice – Rovigo, glass section, since 2016.

Prof. Francesco Gonella

PhD in Physics at the University of Padua, Italy, Excéllence Postdoctorale at Université Laval, Canada. Presently Full Professor of Physics at the Dept of Molecular Sciences and Nanosystems, Venice Ca' Foscari University, Italy.

Research activity with interests in the experimental study of glasses for ICT and for energy technologies, Systems thinking and emergy accounting, study of artistic glass. Author or co-author of about 150 publications in international peer-reviewed Journals, co-author of 3 contributions in encyclopaedias.

Invited lecturer in Universities at the Université Laval (Québec City, Canada), McGill University (Montréal, Canada), Vanderbilt University (Nashville, USA), Cornell University (Ithaca, New York, USA), Martin-Luther Universität, Halle, Germany, Bharati Vidyapeeth Deemed (Pune, India), Tokyo Institute of Technology, Japan, Kyoto Institute of Technology, Japan, Tokyo Institute of Technology, Japan, Shinshu University (Nagano, Japan), Padova University (Italy), Kyoto University, Japan.

Visiting Scientist at the University of Florida (Gainesville, USA) and at Vanderbilt University (Nashville, USA). Visiting Professor at the Tokyo Institute of Technology (Japan). Invited talks in International Conferences in France, Poland, Germany, Canada, Italy, Japan. International awards for research activity: "Marco Polo of the Italian Science" Award (2011).

Sandro Hreglich

Sandro Hreglich, currently retired, graduated in Chemistry at the University of Padua, worked for 40 years at the Stazione Sperimentale del Vetro in Murano: research institute in the field of glass and technological assistance to the glass industry. Its main activities concerned the set up of vitrifiable batches and the identification of new raw materials for the glass industry. He coordinated many national and european applied research projects in the Glass field.

Prof. António Pires de Matos

Degree in Chemical Engineering, Technical University of Lisbon 1962. PhD in chemistry, Cambridge, U.K., 1970. Director of the Chemistry Department of the Portuguese Nuclear Institute from 1992 to 1996 and vice-president of the same Institute from 1996 to 1998. He is Emeritus Coordinator Researcher of the Portuguese Nuclear Institute (now part of the *Universidade de Lisboa*) and Emeritus Invited Professor of the *Universidade NOVA de Lisboa*. He was responsible for the introduction in Portugal of the chemistry of coordination and organometallic compounds of lanthanides and actinides and the Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, a technique with which the first kinetic studies of ion-molecule reactions with protactinium, neptunium, plutonium, americium and curium were made. In 1995 started to be interested in art and science of glass and in 2002 with colleagues from fines arts founded the Research Unit Glass and Ceramics for the arts, VICARTE. He was also responsible for the creation of a Master in Glass Art and Science which started in 2009. In the same year was nominated Fellow of the Society of Glass Technology, U.K.. Coordinated the organization of several meetings of glass and recently an exhibition in Palazzo Loredan, Venice, curated by Francesca Giubilei and Rosa Barovier. He was co-author of over 100 peered reviewed publications in international journals and translated three books of inorganic chemistry to the Calouste Gulbenkian Foundation. In October 2016, the Portuguese Chemical Society gave him the prize Alberto Romão Dias, an award for his career in chemistry. His current research activities at the Research Unit VICARTE are the provenance studies of Portuguese glass and the science and technology of glass applied to contemporary glass art.

Prof. Carlo G. Pantano

Carlo G Pantano is Distinguished Professor Emeritus of Materials Science and Engineering at the Pennsylvania State University. His research accomplishments address the effects of glass composition and processing on the surface composition and reactivity of glass substrates and fiber glasses. He has over 300 journal publications, 6 book chapters and has edited several monographs. Now, he continues glass research, and the supervision of undergraduate and graduate students, in collaboration with two other faculty members (John Mauro and Seong Kim) whose work focuses on glass. He also continues to supervise a glass-blowing studio where students engage in extramural activities and research; several have expressed interest in glass colour. His role in this round-table project is to provide liaison with US glass scientists and companies, to engage PSU students and faculty in relevant projects, and to identify expertise and facilities relevant to research on glass colour and its toxicity.

Prof. John Parker

John Parker was educated in his home town at Boston Grammar School, becoming the Parry Gold Medallist in 1964. His academic career continued at Cambridge University. His Bachelor's degree in Natural Sciences (first class, 1967) was followed by a PhD in Earth Sciences (1970) and two years postdoctoral research. He moved on to the University of Sheffield in 1972 taking a permanent lecturing position in Glass Technology; he became a professor in Glass Science and Engineering before retiring in 2009, while the University also recognised his work with Biomedical Engineering students with an Award for Service. The Institute of Materials awarded him both a Fellowship and a CEng qualification in 1995. He served as a journal editor and was the president of the Society of Glass Technology from 2004 to 2006; his SGT Fellowship in 1983 was followed by an Honorary Fellowship in 2013. He has been secretary of the Coordinating Technical

Committee for ICG since 1996, is responsible for their web pages and serves on the Education Committee; ICG has recognised his contribution by awarding him the WES Turner prize and the prestigious President's Award.
He has researched and published extensively, his output including 7 books, 138 papers/articles and 1 Patent; he writes a monthly article on glass history for the Glass International Magazine. He has given 71 invited talks, many overseas and 70 other conference presentations following research grants awards of over a million pounds. Whilst his interests have been broadly based, glass colour has been a common theme. He currently enjoys lecturing at an ICG Summer School in Montpellier, France and a Winter School in Wuhan, China. He still teaches at the University of Sheffield and holds an honorary position as Curator of the Turner Museum of Glass, giving frequent talks to lay audiences.

Prof. Setsuhisa Tanabe
He received his PhD at Department of Industrial Chemistry in 1993, and is Full Professor since 2008 in Kyoto University. He is the author of 200 original papers, 25 book chapters, and 37 review papers on rare-earth doped luminescent materials for upconversion, fiber amplifier for optical telecommunication and LED phosphors. Plenary or invited speaker at more than 100 international conferences. Chair of Technical Committee of Optoelectronic Glasses (TC20) of International Commission on Glass (ICG) during 2003-2011, member of Steering Committee of ICG since 2013. Visiting scientist at Rutgers University, NJ during 1996-1997, invited professor at University of Rennes in 2010 and 2016. Associate Editor of Journal of Luminescence.
Awards
1994 Research Award of Inoue Foundation for Science.
1995 Research Award by Research Foundation for Opto-Science and Technology.
1996 Young Scientists Award, The Ceramic Society of Japan.
1998 Young Scientists Award, The Chemical Society of Japan.
2002 G.Adachi Award, The Rare Earth Society of Japan,
2003 Marubun Research Award
2009 Academic Award, The Ceramic Society of Japan
2012 2011 JCerS Best Paper Award, The Ceramic Society of Japan
2012 W.E.S. Turner Award, International Commission on Glass (ICG)

Caterina Toso
President of association InMurano, Caterina is the promoter and coordinator of the round-table "The Future of glass colour" – GAS conference 2018.
Caterina Toso was born in a glass-makers family in Murano: she quickly learnt to know and love Murano glass world.
After her MA in International Business (Leeds Metropolitan University – UK) Caterina came back to Murano to take care of Fratelli Toso art gallery and family business. She undertook a long-term project to recover historic archive of Fratelli Toso glass-factory, which is now being re-ordered, studied, digitalized. Caterina also collects information and data regarding Murano families, glass-factories and Murano glass production from the 19th century.
In 2014 she was a co-founder of the association InMurano engaged in safeguarding and promoting local glass heritage and culture.

The Future of Colour Glass

Research Objective and motivation

Artistic glass production in Murano island is currently facing a threatening situation, which involves several aspects ranging from environmental and socio-economic to scientific issues. The goal of the round table is to properly and fully address the nature of the problems related to glass colour and of the present situation due to the prohibition of the use of some toxic compounds. There is no sufficient reliable information regarding the level of real danger, how the environment pollution can be controlled and if solutions are possible without killing the local artistic glass industry. Health and environmental issues are highly relevant and international regulations are now set to take care of related dangers. Traditional and ancient production centres, such as Murano, have been the core of artistic glass production not only economically, but also socially and culturally. It is highly worthwhile to engage in serious and appropriately structured research to determine if it is possible to offer suitable and sustainable solutions to preserve artistic production centres, with their important cultural heritage, while at the same time, satisfying urgent health and environmental requirements. This group of international scholars together with local glass experts aims to give a clear image of the present situation and analyse all possible solutions for the future of local artistic glass centres such as Murano.

Introduction and background

Since ancient times glass compositions in Venice have been a secret that has been carefully protected. Each glass factory used to develop its own secret recipes for colours, recorded and jealously guarded by a trusted person who always kept these recipe books as confidential information. These books - “librii dee partie” - were then passed on from generation to generation.

One of the most interesting and important documents about ancient glass recipes is the so called “Ricettario Darduin”: this mysterious book is a collection of ancient glass compositions selected and collected by Giovanni Darduin and completed by an anonymous successor. It is conserved in the State Archive of Venice, where Luigi Zecchin – an important expert and researcher during the '900, who made a fundamental contribution to glass-art studies - studied it with great interest. Another notable recipe book is “Arte Vetraria” by Antonio Neri which is better known because it was published many times from 1612 onwards. Both Giovanni Darduin and Antonio Neri used their own experience as glass technicians, they took available recipes and verified their results.

The “Ricettario Darduin” sheds new light on the range of colours produced and on the quality of glass produced in the past – covering the period between 1500 and 1650 ca. This was a working tool for glass-makers: a collection of almost three hundreds recipes for preparing different kinds of glass and descriptions of raw materials used. Also, all of the consequential operations to be performed are described.

It describes coloured glasses in particular: different hues of red, yellow, green, black and blue – both transparent and opaque. A large part is dedicated to copper red, ruby glass (with gold), aventurina, chalcedony, lattimo glass and opalescent glass (with arsenic).

This book showcases what Murano's main strength was – complex compositions and the procedures to obtain peculiar glasses and unique colours. Maybe the glass quality was superior in other centres such as Bohemia, but nowhere else was there such a wide range of colours and so many glass types.

Present framework – Research problem

Overview on old compositions and old recipes.

Many old glass compositions and documents (such as the Ricettario Darduin) can help to find sustainable solutions for glass production without toxic substances.

It is worthwhile to look to old recipe books to find possible options.

It is important to know that cadmium, used for red/orange/yellow glasses, started to be used in the beginning of the 1900's. Arsenic and lead, used to give brilliance to white glass and *smalto,* started to be used in in the end of 1600's.

But if arsenic and lead have been substituted in glass compositions – even if with relevant quality loss – it still does not exist any solution to eliminate the use of cadmium. The main issues are related to this particular category of compounds which will be soon forbidden.

Is there any solution to comply with health and environmental issues without killing Murano local artistic industry?

Nowadays local artistic glass centres, including Murano, are threatened by the consequences of new international regulations regarding substances that may pose a health or environmental risk. Many glass factories do not have the budget needed to adapt their production facilities to meet these new regulations, aimed at safeguarding health and environment. Glassmakers do not have sufficient finances to engage in research to find suitable replacements for the recently declared toxic and forbidden compounds in colour glass compositions.

Furthermore, there is a general lack of clarity concerning the research done so far regarding both the best structural changes to be introduced in the glass factories, as well as with respect to which compounds and substances are likely to become forbidden in the near future.

Systematic shared knowledge and accessible information regarding the state-of-art for specific coloured glass production is in turn lacking, along with data regarding health and environmental issues. This seriously hinders an effective national and international response and investigation to identify suitable solutions. Information sharing is critical for identifying clearly specified problems and addressing possible solutions through experimental activity, both in academic laboratories and Murano furnaces.

In fact, no long-term collaborations exist at present between glass producers and scientific/academic world that could either support or implement experimental research aimed at the creation of new colour glass compositions, both environmentally and economically sustainable ones.

Murano glass production overview (2015)

Annual glass tons produced (2015)	
Industrial glass production	1473 tons
Artisan glass production	435 tons

Glass	Industrial production	Artisan production
Crystal Sb	593 tons	305 tons
Crystal As	26 tons	43 tons
Crystal As + Sb	34 tons	16 tons
Smalto + Opalescent	98 tons	0.3 tons
As colorants	63 tons	20 tons
Ruby	9 tons	0.3 tons
Colorants with Cd	89 tons	4 tons
Other	564 tons	26 tons
* Arsenic has now been banned		

REACH

REACH is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals. REACH establishes procedures for collecting and assessing information on the properties and hazards of substances: authorities can ban hazardous substances if their risks are unmanageable. They can also decide to restrict a use or make it subject to a prior authorisation. REACH also determines maximum level of substances allowed in the final product.

Main problems for Murano glass industry: cadmium, selenium, lead, chromium, cobalt, nickel, fluorine, arsenic, antimony.

Yellow glass: cadmium sulphide (CdS) has been the choice of glass makers to obtain bright yellow coloured glasses. However, cadmium is extremely toxic and is classified as a carcinogen. It is listed to be banned in the next few years.

Orange/Red: A solid solution of CdS-cadmium selenide (CdSe) has been traditionally used to obtain hues of orange and red glass by tuning their band gaps with the composition.

No acceptable solutions to substitute cadmium have been identified so far.

White opaque glass and opalescent glass (used for *filigrana* and other complex traditional techniques)

Arsenic has already been forbidden and since then glass-factories achieved the preparation of glasses with new compositions without arsenic based partly on recipe books and on other opaque glasses used now in the industry. But the following problems have been highlighted:

1) lower quality colour and opacity (less brilliant colours, non-uniform opacity)
2) uncontrolled modification of the degree of opacity and staining of glass during complex glass processing that require repeated heating and cooling of the artefact (i.e. filigrana, reticello, lamp work, fusing)
3) Greater quantity of scrap items due to breakage and unwanted colourings, that inevitably results in an increase in the final cost of production.
4) longer glass processing times of the same glass ware, that cause productivity reduction.

Yellow, orange and red glass with cadmium

Traditionally, yellow glasses had been obtained staining the glass with silver and by the formation of poly-sulphides in the glass matrix while gold, copper and tellurium had been used for obtaining red glasses. Hues of the above colours had been obtained by varying the size of the metal nanoparticles in glasses by glass houses as well as research laboratories. The difficulty in controlling the size and hence the colour using metal nanoparticles has not gained much popularity among artists. Since the beginning of 20th century in Murano, cadmium sulphide (CdS) in conjunction with cadmium selenide (CdSe) has been used in the industry and glass studios to obtain hues varying from yellow to red. Glasses with CdS-CdSe are not only easy to process but also provide a large scope for varying the colour of the glass. However, as cadmium is carcinogenic, its use without using expensive scrubbers is being prohibited worldwide, due to the high cost, scrubbers can only be afforded by factories with high glass production. Application of yellow pigments containing solid solutions of two perovskites had been used in glazes. Several yellow pigments are stable at high temperatures which might be useful for obtaining yellow colour in glasses. However, as far as we know, no such systematic study is available. On the other hand, various thin film coating techniques such as dip coating, spin coating, spray pyrolysis etc. have been effectively used by both artists and scientists to obtain coloured glasses.

White opaque glass

Opacity in glass is the result of the precipitation of crystalline or colloidal compounds during the cooling process which impede the transmission of light. From earlier times, in which antimony-based opacifiers were used, the transition to the preferential use of tin-based compounds was observed. The first elements used as opacifiers in Murano were lead and tin made by their calcination (lead-tin calx). According to Marco Verità a mixture of lead and tin in the proportions of 1/2 to 1/1 was added to the transparent glass, resulting in formation of a white opaque glass due to the dispersion of cassiterite microcrystals. This type of glass was known in Venice by the name of *lattimo*. Later in 1527, a new technique called *filigrana* was invented in Murano which used rods of transparent glass with a core of *lattimo*. Citing Marco Verità "Lead tin calx continued to be used in Murano until the 19^{th} century, partially replaced by other opacifiers such as calcium antimonate (from middle of the 16^{th} c.), calcium phosphate (bone ash) (second half of the 15^{th} c.) and lead arsenate (from 1693)." Until recently several studios and factories used canes for the technique of *filigrana* where the white opacifier was lead arsenate (known as *smalto*) which is now forbidden due to its toxicity.

Research hypothesis

1. New compositions

Identification of new compositions and techniques to eliminate toxic compounds used to colour glass.
Search for alternative raw materials to those already banned or in the process of exclusion by ECHA (European Chemical Agency) such as arsenic oxide, cadmium sulphide and potassium dichromate. In particular, alkaline phosphates were identified in place of arsenic for the production of opaque glass and copper oxide as an alternative to the use of selenium and cadmium sulphide for the red colour. These studies have given positive results as regards the drastic abatement of emissions of polluting agents into the environment. However, the following points, emerged from tests carried out at the Murano glassworks, should also be highlighted.

Red Glass:

- Copper ruby: very intense colour which is difficult to control
- Gold ruby: colour is not a pure red since some blue is also present. It is also more difficult to obtain an intense colour
- Se. It yields red but it is very volatile and it is difficult to get the intensity that CdSe produces.
- Other additives which yield reds under certain conditions - according to Weyl: cobalt, cuprite, iron, neodymium, nickel, uranium in lead glass.
- REs such as neodymium are expensive and give more pastel shades. They do give sharp absorption edges though.

With the aim to assess new strategies to follow for the development of the next generation of red glasses, we believe in an approach that synergistically involves the study of new pigments and their formation/stability in glass. In this regard, we would like to describe an approach that starts with the analysis of new red inorganic pigments. We agree that the main problem is the replacement of Cd, and one strategy could be the precipitation of semiconductors with small band gaps (in the bulk phase) controlling the size to take advantage of the quantum size effect to tune the colour output. We will introduce some quantum semiconductors that could offer possibilities such as $CuInS_2$, CuAgS and Ce_2S_3. Even if more complex, also other compounds (such as bismuth-based semiconductors) may be promising, but an experimental work is required to assess the stability, the reactions and the colour rendering in glass.

Yellow Glass:

Yellows have been made using the following additives: TiO_2-CeO_2; silver nanoparticles (cf copper and gold) give a yellow-orange colour; iron-sulphur amber - yellow if sufficiently dilute.
Other semiconductor particles with a similar band gaps to Cd (S,Se) exist (directly linked to the colour because band gap defines the wavelength of the absorption edge) but some have their own toxicity issues. We need to assemble a list of possibilities e.g. mercury sulphide, gallium phosphides/nitrides used for red & yellow photodiodes.

White opaque glass:

- Study of the traditional white opaque glasses produced with lead-tin calx used before lead arsenate.
- Preparing glasses using calcium phosphate compounds as opacifier.
- Using other opacifiers currently applied in industry such as calcium fluoride, zirconium oxide and titanium oxide, among other compounds. As far as we know, these have not yet been tried and evaluated for their suitability for *filigrana* technique decoration in Murano.
- Reflectance, COE (coefficient of expansion) and viscosity properties of these experimentally produced glasses will be compared with that of lead arsenate white opaque glasses. The batch compositions will be adjusted by varying the quantities of the compounds used as each one contributes to the COE and viscosity differently.

It is important to underline that it is not only sufficient to set up new compositions but also to control atmosphere conditions and test the workability of the new glass.

2. Structural systemic adjustments

- What structural adjustments can be implemented to cut down enough pollution levels during glass melting?
- Is it possible to improve the technology for cleaning flue gases and the working environment for glass blowers?

Filters used in Murano:

Baghouse, bag filter (BF) or fabric filter (FF) - it is an air pollution control device that removes particulates out of air or gas released from commercial processes or combustion for electricity generation

Those filters can reduce pollution levels between 95% and 98%: the main problem is to monitor functioning and maintenance of the filters.

3. Relocation of melting furnaces

If any other solution is arrived at, and both empirical and scientific research show that there are no suitable solutions to adapt Murano production facilities to new health and environmental regulation: is it possible to bring the glass melting process outside Murano?

Problems and issues about this solution:

- Are there any consequences for the colour of red/yellow glasses after re-melting? The danger of re-melting is that the particles may grow and change the colour – in particular large particles may make a red glass turning brown.
- Is toxicity completely absent when it is remelted?
- Would it be worth looking at the methods used to introduce colour by Glass Artists elsewhere in the world e.g. rolling a clear glass gather in coloured glass powder?
- The majority of Murano glass-factories do not have economic resources to move their own melting furnaces somewhere else.

Miscellaneous

1. Pigments

By considering the replacement of the yellow/orange/red glasses based on the solid solution of cadmium sulphide and selenides (CdS-Se), the development of new pigments with suitable colours and low toxicity is an important topic which deserves to be explored. The peculiar optical properties of CdS-CdSe pigments, arising from the unique spectral shape of absorption, make their replacement still a challenge. In this view, in the last decade, new inorganic yellow/orange/red pigments with interesting features have been proposed. An overview of the most promising classes of pigments, such as oxides and oxynitrides, should be addressed.

2. Glaze industry

We also believe it is worth considering the glaze industry (for pottery). Their glass bases have quite different compositions and different colour palettes may be available. Temperatures used are way lower, but their reds are also currently CdSe based and it may be useful to consider solutions they are adopting.