APPENDIX 6 - Chemistry

It was felt that some recognition should be given to the chemistry of glass, as part of the technology, as glass is in fact initially formed by a chemical reaction. Furthermore some of the terms popularly used are only infrequently defined, and some misconceptions have been found as to the derivation of some compounds.

Initially it is very likely that the process was fairly empirical – if a 'recipe' was found that worked it would probably not be altered, unless circumstances changed. As the chemistry behind the processes became better understood, then controlled experimentation could result, leading to a much more consistent product.

Following this, it is evident that at some stage the works at Nailsea included the means of producing the chemicals required on an industrial scale on site. An extant billhead implies that there was indeed a surplus to the needs of the glassworks that could be sold on the open market.[49]

The following is an attempt to address these points in simple terms, but for more detailed, but still comprehensible, expositions see Frank 1982 or Vose, 1980, for example.

Definitions

In the Hutchinson *Dictionary of Science*, 1994, ***glass*** is described as a "transparent or translucent substance that is physically neither a solid or a liquid. ... It is made by fusing certain types of sand (silica): this fusion occurs naturally in volcanic glass [obsidian]." It is well attested that glass comes into a class known as a "super-cooled" liquid, and that this accounts for many of its physical characteristics – for further details see Vose, 1980, pps 21-25, for example.

Hicks, 1983, p.425 writes, "**Glass.** Whilst glass varies widely in its composition, essentially it consists of a mixture of silicates which have not crystallized out on cooling from the molten state. ... Common glass, such as that used in windows, has the approximate composition: $Na_2SiO_3.CaSiO_3.4SiO_2$. The physical properties of glass depend on the proportions of the various silicates present."[50]

We are only concerned with simple glasses here, as lead crystal and other more sophisticated glasses were not, as far as can be determined, made at Nailsea, certainly not in commercial quantities.

N.B. It should be noted that the definition of 'Alkali' in the Hutchinson *Dictionary of Science* is "in chemistry, a compound classed as a base that is soluble in water. ... The hydroxides of metals are alkalis; those of sodium and potassium being chemically powerful; both were historically derived from the ashes of plants. The four main alkalis are sodium hydroxide (caustic soda, NaOH); potassium hydroxide (caustic potash, KOH); calcium hydroxide (slaked lime or limewater, $Ca(OH)_2$); and aqueous ammonia ($NH_{3(aq)}$). ... Alkalis react with acids to form a salt and water (neutralization)."

However, in the Corning Museum of Glass *Glossary*[51] it is defined as, "Alkali : In glassmaking, a soluble salt consisting mainly of potassium carbonate or sodium carbonate. It is one of the essential ingredients of glass, generally accounting for about 15-20 percent of the

[49] SRO D/B/bW 2349: Coathupes &Co., Manufacturers of Crown Window Glass & Alcalis, [*sic*], (Bristol, 20th Feb. 1846) – See Appendix 11

[50] Hicks, J, 1982, pps. 424-5

[51] From the Corning Museum of Glass website

batch. The alkali is a flux, which reduces the melting point of the major constituent of glass, silica."

Compounds

Substance – common name	**Chemical name**	**Chemical formula**	**Derived from**
Alkali (see **N.B**. above) Potash Soda ash	See below under individual entries	See below	See below
Black Ash	Sodium carbonate	Na_2CO_3	$Na_2 SO_4$ heated with coal and limestone. Soda extracted by leaching
Caustic potash	Potassium hydroxide	KOH	Similar to caustic soda
Caustic soda	Sodium hydroxide	NaOH	Slaked lime + dilute sodium carbonate solution +heat
Ferric Oxide	Ferric Oxide	Fe_2O_3	Haematite
Lime	Calcium oxide	CaO	Burning limestone in a kiln
Lime(stone)	Calcium carbonate	$CaCO_3$	Limestone, but also chalk
Nitre, Saltpetre	Potassium nitrate	KNO_3	
Oil of Vitriol, Vitriol	Sulphuric Acid	H_2SO_4	
Potash	Potassium carbonate	K_2CO_3	Land plants (ash)*
Salt	Sodium chloride	NaCl	
Salt cake	Sodium sulphate	Na_2SO_4	Salt treated with sulphuric acid
Silica	Silicon dioxide	SiO_2	Quartz as Common sand
Slaked lime	Calcium hydroxide	$Ca(OH)_2$	Lime plus water
Soda ash	Sodium carbonate	Na_2CO_3	Marine plants (ash) esp. kelp†

*Wood-ash from beech was favoured[52], and ash from bracken was also used.[53]

† Also, the Concise Oxford Dictionary gives "**glass-wort**, plant of genus *Salicornia* or *Salosa* formerly burnt for use in glass-making." [It is also known as 'marsh samphire'[54]]

[As chemical engineering developed, less reliance was placed on plant derived compounds and synthetic compounds produced by reactions on an industrial scale were employed. These will not be detailed here. However, the increased purity of the constituents meant that certain

[52] Adkins, L and Adkins R, 1998: p.268
[53] Burgoyne, I and Scoble, R, 1989: p.3
[54] Reader's Digest *Wild Flowers of Britain,*1997, p.95

elements that had naturally been in the earlier product, and were in fact beneficial, had to be re-introduced, examples being lime, alumina and magnesia.[55]]

Hicks, 1983, p.420, under **Silicon Dioxide, Silica, SiO_2** says, "This compound occurs naturally as quartz and sand and also as flint, opal and agate." He points out that "pure silica is colourless, but sand is usually coloured yellow or brown by ferric oxide impurity."

Reactions

Hicks, *Ibid.*, gives typical reactions, [of silica] "important in glassmaking", as, when heated strongly:

"$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2\uparrow$"

[Silica + sodium carbonate gives sodium silicate with carbon dioxide given off.]

"$SiO_2 + Na_2SO_4 = Na_2SiO_3 + SO_3\uparrow$"

[Silica + sodium sulphate gives sodium silicate with sulphur trioxide given off.]

On p.424, Hicks, *Ibid.*, writes, "It [glass] is made by melting together silica (i.e. sand) with calcium carbonate or oxide and sodium or potassium salts, usually the sulphate and the carbonate:

e.g. $SiO_2 + CaCO_3 = CaSiO_3 + CO_2\uparrow$

$SiO_2 + K_2SO_4 = K_2SiO_3 + SO_3\uparrow$ "

The alkali acts as a flux, bringing the melting point temperature down, while the lime(stone) acts as a hardener. If the sodium compound predominates the melting point will be lower, relatively, which means less fuel would be consumed in the heating and working processes; it will not be lowered to the same extent if the potassium compound is present. The addition of scrap glass, commonly called 'cullet', also assists considerably in lowering the melting point of the raw materials if it is included in the mix.

Pilkington give the following, under 'Chemistry of Glass'[56], "Important glassmaking chemistry: the basic reactions:

$$Na_2CO_3 + SiO_2 \xrightarrow{1{,}500^\circ C} Na_2SiO_3 + CO_2\uparrow$$

$$Na_2SiO_3 + xSiO_2 \xrightarrow[\text{Digestion}]{Na_2SO_4} (Na_2O)(SiO_2)_{(x+1)}$$

For practical and economic reasons, the high melting point and viscosity of silica is reduced by adding sodium oxide (a flux) in the form of a carbonate."

Traces of other elements either added accidentally as impurities in, say, ash, or later deliberately, such as manganese, could affect the chemical stability of the glass, for example. They might also decolourise it or colour it depending on the appropriate element or compound being added. It is not considered necessary to explore the chemistry of these reactions any further here.

It can be seen that the processes were not good either for greenhouse gasses (CO_2) or acid rain (SO_3 combines with water to form sulphuric acid.) In addition the "stack" at Nailsea gave off gaseous hydrochloric acid, which, understandably, gave offence under certain weather conditions.

[55] Vose, p86
[56] From Pilkington Glass website

APPENDIX 7 - English Heritage Report

Centre for Archaeology Report 16/2004

Scientific Examination of Glass and Glass Working Materials from Nailsea, Avon

Gareth Hatton

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Centre for Archaeology Report 16/2004

Scientific Examination of Glass and Glass Working Materials from Nailsea, Avon

Gareth Hatton

Summary

Historical documents show that the glassworks at Nailsea were established in 1788 and continued until 1874. An assemblage of glass and glass working waste (2.8kg) was submitted for examination and subsequent analysis. Samples to represent the range of colours, forms and sizes present were selected for chemical analysis. It was determined from these analyses that colourless glass was produced on site. The glass is a soda lime silicate glass.

Keywords

Glass
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