GLASS MAKING TODAY

Edited by P.J. Doyle

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GLASS-MAKING TODAY

An introduction to current practice in glass manufacture

Compiled and edited by

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GLASS-MAKING TODAY

Foreword

by
Charles Thorpe,
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There are many, perhaps too many, articles on special aspects of glass technology published every month in the scientific and trade press and finding time to read enough of them to feel confident of keeping abreast of technical developments is not an uncommon problem. Sound practical books covering glass manufacture in general, however, are not nearly so numerous, perhaps because the people who might write them, having other commitments, cannot find the time to undertake the daunting task of compressing their know-how into the necessarily-numerous pages of a book.

Whatever the reasons, the fact is that since Hodkin and Cousen's classic tome appeared in 1925, no English author has ventured to produce a book on glass manufacture intended mainly for use by people working in, or closely associated with, the glass industry itself.

I was therefore particularly pleased to support the work that has gone into producing "Glass-making Today", which represents a distillation of the practical experience of several authors, including many friends of long-standing, for the benefit of anyone concerned with the glass industry.

The result is a technically first class, and readable, book that should prove of value to a wide range of people who work in the industry or service it, and also of real interest to anyone concerned with the art (and craft) of making glass.

Preface

"Glass-making Today" is a compilation of information of present-day practice in the commercial manufacture of glass which, it is hoped, will be helpful to young graduates entering employment in the glass industry, to experienced technologists in other industries who need a succinct guide to glass-making processes for some research project or sales venture and to the general reader who merely wishes, for his own pleasure, to gain insight into the processes currently used to manufacture one of the oldest and yet most modern of engineering materials.

The technology of modern glass-making is essentially the same in all the major industrial countries and it is hoped that the book will be found useful throughout the English-reading world but where geographical considerations have required the data to be specific, for example in the case of the availability of raw materials, the slant has been towards conditions obtaining in the United Kingdom.

The idea for the project that has resulted in the present publication originated with Denis Rider who, sadly, died in August 1977 before it could come to fruition. I met Denis in the early 1960's when he was Director of the Glass Manufacturers Federation and he first made me conscious of the fact that, while there were several excellent text books on the properties and applications of glass as a material, the only reasonably comprehensive books describing glass manufacturing processes were outmoded, or firmly based on American practice, or both. When in 1975 Portcullis Press invited Harold Rawson, now Professor of Glass Technology in the University of Sheffield, Oscar Feldman, Assistant Director-Technical of the Glass Manufacturers Federation, and myself to discuss with them new ventures that Portcullis might usefully undertake, the position had not substantially improved and the possibility of meeting that long-felt need came readily to mind.

It was apparent that such a book could be produced only on a collaborative basis and various people known to have had considerable practical experience in the glass industry were invited to write the sections relevant to their VIII PREFACE

expertise. The plan was to cover, at least in outline, all the major aspects of producing glass commercially with particular emphasis on techniques and processes common to all types of manufacture. The properties and subsequent processing of glass are described only incidentally with indications of where further, more detailed, information is readily available in the literature.

The result of this exercise is "Glass-making Today", which has been made possible by the knowledge, hard-work and tolerance of the contributors, whose names will suffice to recommend them to anyone even only slightly acquainted with the British Glass Industry, by the willing co-operation of all the companies and organisations who were approached for help in any way, and by the imagination and faith of the publishers, which it is hoped may be rewarded in the fullness of time. To them, to my Director of Research, Charles Thorpe, to the Council of the British Glass Industry Research Association and to all those associated with the publication of the book I am extremely grateful and especially to Denis, albeit posthumously, for his original inspiration.

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1 Raw Materials

1.1 SAND

1.1.1 Introduction

The massive expansion of the glass industry over the last 60 years has, of necessity, led to a remarkable growth in the demand for sand. Whereas the consumption in 1916 was just over 300,000 tons, in 1974 it was more than 2 million tons.

The first systematic survey of British glass sand reserves was made by Boswell in 1916.^(1,1) In this he listed 35 sources but gave no indication of the quantities produced from each one. As the total sand used in 1916 was 325,000 tons and over 100,000 tons was imported, it can only be concluded that some, if not all, of the operations must have been very small by present day standards.

At the present time, all the glass sand produced in the U.K. comes from five suppliers, and is extracted from eight quarries. Here the sand industry has followed the pattern of industry in general, in concentrating production into big units. This was inevitable as the demand became too large for the small quarry operator without the resources to invest in mechanical quarrying equipment and sophisticated processing plant. Large scale production came late in the U.K., principally because of the ready availability of cheap, high quality continental sands, and the large quarry worked by Joseph Boam near King's Lynn was still dependent on manual labour as late as 1951. During the last 20 years, however, mechanical working has become general, and this has meant mechanisation in the plant used for sand handling, and the introduction of more sophisticated processes for purification (beneficiation).

1.1.2 Specifications

The sands used in glass-making consist essentially of quartz grains within a size range which ensures that coarse and fine particles are present in minimal amounts. Coarse grains reduce the melting rate, or appear as "stones" in the finished glass. Fine grains lead to refining problems or carry through the furnace into the regenerator system causing damage to the brickwork.

Mineral grains other than quartz are always present in sands. Not all of these are detrimental. Felspathic minerals contribute to the alumina content of the glass, and the oxides combined with the alumina, such as silica and the oxides of sodium and potassium, are compatible with the other constituents of the batch. However, heavy mineral grains which contain metals such as iron, titanium and chromium are deleterious in contributing to the colour if a colourless glass is being made, and large grains of minerals such as chromite are refractory enough to remain as specks in the finished glass.

The first specification for glass-making sands appeared in the *Journal of the Society of Glass Technology* in 1935.^(1,2) This was revised in 1943.^(1,3) and a British Standard Specification—BS 2975—was published in 1958.^(1,4) The Standard is in process of revision but in the meantime the Glass Manufacturers Federation has produced a document.^(1,5) setting down preferred specifications for sands used in the various categories of glass manufacture.

BS 2975 specifies the particle size, the minimum silica content, and maximum contents for iron, titanium and chromium. The particle size requirement is that 80% of the sand grains should fall between 420 microns (36 BS mesh) and 150 microns (100 BS mesh). There should be nothing coarser than 1,000 microns (16 BS mesh), and not more than 2% coarser than 600 microns (25 BS mesh). In the smaller particle size range, not more than 5% should be finer than 125 microns (120 BS mesh).

Three levels of purity are specified, A, B and C. Grade A sand, suitable for the manufacture of high grade optical ware, should contain no more than 0.008% Fe₂O₃, 0.030% TiO₂ and 2 ppm Cr₂O₃. Grade B sand, suitable for high grade domestic and decorative glassware, should contain no more than 0.013% Fe₂O₃ and 2 ppm Cr₂O₃. Grades A and B should contain a minimum of 99.5% SiO₂.

Grade C sand, suitable for the manufacture of colourless containers etc., should have a maximum Fe_2O_3 content of 0.030% and not more than 6 ppm Cr_2O_3 . There is a proviso that the Fe_2O_3 specification can be relaxed to 0.035% maximum if the sand contains less than 2 ppm Cr_2O_3 . A minimum SiO_2 content of 98.5% is specified.

This specification refers only to sand used in the manufacture of colourless glass, and many thousands of tons of sand (with contents of colouring elements well outside the limits specified) are used in the manufacture of flat glass and coloured containers.

1.1.3 Glass Sand Production in The United Kingdom

There is very little sand in the British Isles which compares in quality with that found in a number of deposits on the Continent. Those sources of high purity sand which are known—Muckish Mountain in Donegal, and Loch Aline on the Sound of Mull—are located in relatively remote areas. Of the deposits noted by Boswell, the Greensand and the Carboniferous deposits associated with the coal measures (Millstone Grit) are still important sources of glass-

making sand. For the manufacture of colourless glasses, these sands require some treatment other than the traditional procedures of washing and screening.

Because of the availability of cheap continental sands mechanical quarrying and sophisticated processing were introduced late in the U.K., much later, for example, than in the U.S.A. The first plant set up to process sand by a chemical treatment began operation on a Lower Greensand deposit near King's Lynn in 1936. (1.6) The cessation of supplies from the Continent in 1940 gave a tremendous boost to the production of indigenous sands, and a considerable amount of exploration was carried out during the war years. By 1945 production was well established on a Lower Greensand deposit near Redhill, and a battery of shaking tables was installed in 1946 for the removal of the heavy mineral content. Investigation of the deposits in the south-east showed that the sands in this area contained sufficient chromium to give a visible colour in glass which had a low iron content. This impurity is not present to the same extent in continental sands nor, in fact, in the Lower Greensand in the Norfolk area. Whilst the sands were acceptable under war time conditions, it was realised that the beneficiation of native sands was essential to meet the post-war resurgence of competition from the Continent.

A more effective means of removing the heavy mineral fraction was to subject the sands to froth flotation, a process familiar in the concentration of non-ferrous metal ores, but one which had not found an application in sand processing in this country. The first plant of this kind was installed at Redhill in 1949. (1.7)

The chemical process operated at King's Lynn was aimed at the removal of ferruginous surface coatings from the quartz grains. It was based on the dissolution of the iron oxide in a warm, acidified oxalate solution, in the presence of ferrous sulphate. The principle of leaching with an acid solution under reducing conditions, formed the basis of a number of processes for sand beneficiation, $^{(1.7,1.8)}$ and one of these in which hydrofluoric or sulphuric acid is used with the addition of hydrosulphite ion (S₂O₄--), as either the sodium or the zinc salt, has been operated on a large scale at the King's Lynn and Redhill sites for over 20 years. The basic chemistry was discussed in a paper by Segrove^(1.7) in 1956.

In 1959 a plant was erected near Oakamoor in Staffordshire to work the third grit of the Millstone Grit series. This requires crushing and milling and for this duty an Aerofall mill, which operates as an autogenous grinder, was introduced. (1.9) The sand produced in this way was surface cleaned in attrition machines at a controlled pH. (1.10) The principle of surface cleaning, either by leaching or by attrition, followed by froth flotation to remove the more refractory minerals containing colorants, has been adopted in other U.K. plants of more recent date. Reviews of sand processing techniques were published by Gregory (1.11) in 1964, and Segrove and Stanyon (1.12) in 1969.

With the increasing need to process lower grade materials to extend the life of existing reserves of sand, interest has centred more recently on the use of strong acids in high concentration and at elevated temperatures. A process in which 20% hydrochloric acid is used for sand leaching at around 100°C and

in which the acid is recovered for re-cycling was patented^(1.13) in 1971, and a plant to work the process on the Millstone Grit deposit at Oakamoor was installed in 1970. More recently, and because of the difficulties experienced in handling hydrochloric acid, the plant has been converted to using 30% sulphuric acid.

The use of sulphuric acid for sand leaching was the subject of a series of U.S. patents in the early '30s, and an account of a plant erected in Ohio to work the process was published by Sawyer^(1.14) in 1947.

In addition to the processes mentioned above, a whole host of possibilities have been canvassed over the years, and many have surfaced in the form of patent applications. The choice of a processing circuit must be decided primarily by the mineralogy of the particular deposit which it is intended to work. For each specific duty there may be a number of alternatives known to the mineral engineer. A final choice can only be made on the basis of technical merit, feasibility and economics.

1.1.4 Present-Day Sources of Glass-Making Sands

The sources of sand in the U.K. must be considered in relation to the glass-making centres. The chief of these are the London area (now decreasing in importance), S.E. Lancashire, S. Yorks and Central Scotland. Other localities important in the glass industry are the Stourbridge area and the N.East coast, but the products are highly specialised and require sand of a purity not readily available in the U.K. The tonnages are relatively small, and requirements are met mainly by importing Continental sands.

Sand is supplied to the glass industry from deposits which vary greatly in geological age. The Millstone Grits which date from the Carboniferous period are the oldest, whilst the Glacial are the most recent. Next in age to the Millstone Grits are the Greensands from the Cretaceous period. These are much closer in age to the Millstone Grits than they are to the Glacial sands.

Deposit Locality Use Tonnage Greensand Loch Aline Mainly colourless glass 120,000 (Cretaceous) Redhill/Reigate Mainly colourless glass 420,000 King's Lynn Mainly colourless glass 550,000 Millstone Grit Oakamoor Mainly colourless glass 310,000 (Carboniferous) Some flat glass Devilla Mainly colourless glass 100,000 Glacial and South East Flat glass 300,000 Recent Sands Lancashire Chelford Mainly coloured glass 290,000 Some flat glass Coloured glass Messingham 172,000

Table 1.1

As a consequence of this the Glacial (and Recent) sands contain far more alumino-silicates, such as felspars and micas, than do the older sands. This means that the silica contents are 95-97% against 98-99.5% in the older sands, and the alumina amounts to 1-3%.

From the most recent figures available in 1974 the glass industry consumed around two and a quarter million tons of sand. Of this 48% was taken from the Greensand deposits, 34% from Glacial deposits, and the residue from the Carboniferous grits.

The deposits currently being worked as glass-making sands and their geographical locations relative to the glass-making centres are shown in Fig. 1.1.^(1.15) The estimated tonnages produced during 1974 from the various localities are given in Table 1.1.

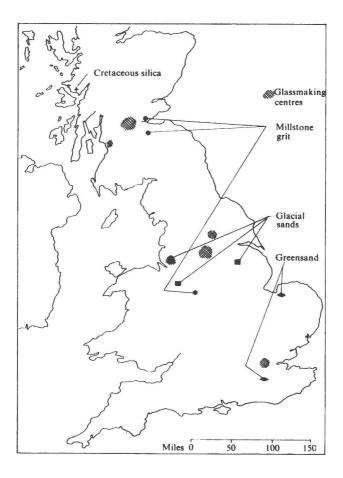


Fig. 1.1. UK sources of glassmaking sands