GLASS TECHNOLOGY

Developments Since 1978

Edited by J.I. Duffy

GLASS TECHNOLOGY

Developments Since 1978

NOYES DATA CORPORATION
Park Ridge, New Jersey, U.S.A.
1981

Library of Congress Catalog Card Number: 80-26045
ISBN: 0-8155-0838-7
Printed in the United States

Published in the United States of America by
Noyes Data Corporation
Noyes Building, Park Ridge, New Jersey 07656

Library of Congress Cataloging in Publication Data

Duffy, Joan Irene, 1950-
Glass technology.

(*Chemical technology review* ; no. 184)
Includes index.
1. Glass manufacture--Patents. I. Title.
II. Series.
TP858.D83 666'.1'0272 80-26045
ISBN 0-8155-0838-7

FOREWORD

The detailed, descriptive information in this book is based on U.S. patents, issued beginning with January 1979, that deal with glass technology.

This book is a data-based publication, providing information retrieved and made available from the U.S. patent literature. It thus serves a double purpose in that it supplies detailed technical information and can be used as a guide to the patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced commercially oriented review of recent developments in the field of glass technology.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring these durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The table of contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

16 Reasons Why the U.S. Patent Office Literature Is Important to You

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source. Most important technological advances are described in the patent literature.

2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."

3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.

4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.

5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.

6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.

7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.

8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.

9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.

10. Obtain licenses—many U.S. chemical patents have not been developed commercially.

11. Patents provide an excellent starting point for the next investigator.

12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.

13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.

14. Identifying potential new competitors.

15. It is a creative source of ideas for those with imagination.

16. Scrutiny of the patent literature has important profit-making potential.

CONTENTS AND SUBJECT INDEX

INTRODUCTION

The term "glass" means an inorganic product of fusion which solidifies to a rigid, noncrystalline condition upon cooling. Most of the commonly used glasses are silicate glasses. These include container glass, plate glass, borosilicate glass, fused silica, special high-melting glasses, glasses designed specifically for subsequent devitrification, sodium silicates, fiber glass, glass wool, slag wool, and rock wool.

Various techniques are presently being used to manufacture flat sheet glass. Typically, premixed glass-forming materials are fed onto the surface of a bath of molten glass contained in a furnace. In the fuel-firing of the regenerative tank type furnaces, the materials are melted by hot gases from flames playing across the furnace above the glass surface. In the more modern electric furnaces, heat is produced by passing electric current through the bath of molten glass between electrodes immersed in the glass. Also, a combination of both heating methods is sometimes employed.

The furnaces described above assume various shapes. Early regenerative, fuel-fired, tank type furnaces were generally horizontal and rectangular in shape with raw material received in one end and molten glass formed in a continuous sheet on the opposite end. This furnace at one time enjoyed considerable popularity in view of the abundance of relatively cheap natural gas energy resources. However, as natural gas fuel became scarce and therefore expensive, the energy consumption deficiencies of the regenerative furnace soon became apparent.

In particular, the horizontal regenerative furnace experienced considerable heat loss because of its relatively large exposed cross-sectional areas. Therefore the trend in recent years has been to employ vertical furnaces. These furnaces are characterized by smaller cross-sectional area, and therefore less heat loss. However, these furnaces likewise have not been without problems. A perennial problem with electric furnaces has been heat localization around the electrodes, and the integrity of the furnace wall surrounding the localized electrode heat pockets. Furthermore, normal electrode wear requires regular replacement, which has resulted in shutdown of the furnace.

A glass sheet is tempered by a two-step process in which the glass is first heated to an elevated temperature and then is cooled very rapidly to a temperature below the strain point. Tempering provides glass sheets with a stress pattern in which the glass sheet develops a thin skin of compression stress surrounding an interior stressed in tension. Such a stress distribution makes the glass sheet much stronger than untempered glass so that tempered glass is less likely to shatter when struck by an object. Contained in this volume are a number of processes dealing with improved methods of strengthening and toughening glass, as well as apparatus designed to handle the glassware more efficiently and with less breakage.

The significance of the role to be played by optical fibers in information transmission systems is no longer in dispute. The emphasis of research and development programs in this field has shifted from that of proving practicality to one of improving transmission efficiency. An active area, which has been particularly fruitful in yielding such improvements, involves the reduction of losses in optical fibers so that they may be used for long distance transmission. The lower the optical losses in such fibers the less frequent the need for multiple optical repeaters and, consequently, the cheaper the cost of the total system.

Cladded core fibers generally consist of a fiber core and cladding composed of materials which have been selected so that the refractive index of the core is higher than the refractive index of the material forming the cladding.

In self-focusing fibers, the index of refraction decreases from the center of the core (again cylindrical) to the periphery thereof. The refractive index along the radius of the cylindrical cross section of the core is often pseudoparabolic. If the radial gradient is sufficiently large in its absolute value, all the light rays (visible or invisible) are refocused and, because they are unable to escape from the fiber, are propagated by it without any losses.

This book describes the syntheses and treatment of glasses, glass fibers and glass-ceramics and presents formulation and evaluation data for a variety of processes presented in the U.S. patent literature from January 1979 through mid-1980. The processes are grouped according to their major use, but it should be recognized that many of these formulations may be used for other applications as well.

GLASSMAKING

MELTING

Glass Batch Wetting and Mixing Apparatus

Glass batch in its usual form is a mixture of finely-divided solids which are thoroughly mixed and delivered to a refractory furnace by a system of hoppers, gravity flow chutes and other positive displacement conveyors. Since the batch is a finely-divided material, severe dusting conditions are commonly encountered when the batch is exposed to the high velocity hot gases of the melting furnace.

Additionally, the glass batch is extremely abrasive and will erode even the hardest of materials in a relatively short time where it frictionally contacts the moving parts of conventional positive displacement conveyance means, such as screw conveyors, augers or the like.

A.D. Heller; U.S. Patent 4,172,712; October 30, 1979; assigned to Dart Industries, Inc. describes a structural arrangement wherein the typical hopper of a glass furnace charger is enlarged to such an extent that it will appropriately accommodate a mixing arrangement. The principal mode of movement through the mixer, therefore, continues to be that which is common to the glass furnace charger, i.e., gravity.

Mixing action within the hopper is achieved by means of two rotating shafts having uniquely structured agitating means positioned therearound. These rotary agitators tend not only to mix the batch, but to move same toward the center of the hopper during the mixing action.

Furthermore, responsive to the active feeding action of the charger itself, suitable circuitry is designed to provide a uniform and constant flow of fluid to spray heads positioned above the hopper.

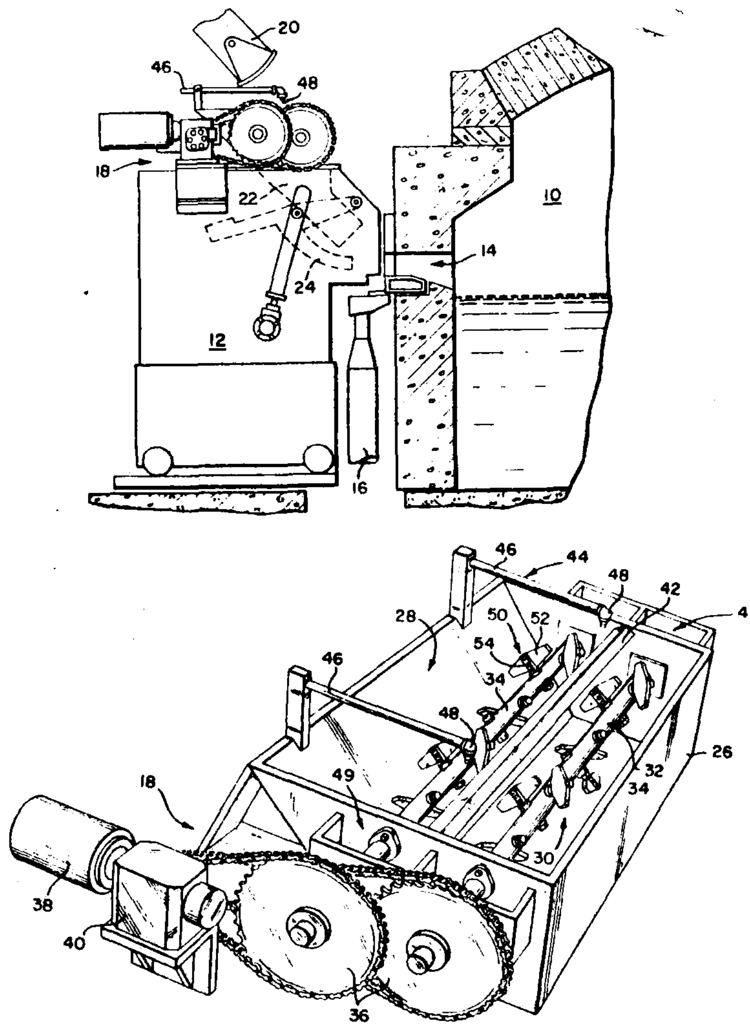
Accordingly, as new batch enters the inlet opening of the hopper, such is thoroughly wetted to a degree that will assure a desired wetness level as same exits the charger into the glass furnace.

Referring to the figures in which like numerals have been used to designate like components, Figure 1.1a shows the relationship between this apparatus and a typical glass melting furnace **10**.

Figure 1.1: Glass Melting Furnace and Furnace Charger with Mixing Apparatus

a.

b.



(a) Side elevation view
(b) Top view of mixing apparatus

Source: U.S. Patent 4,172,712

Adjunct to the melting furnace **10** is the glass furnace charger **12** which is movably mounted for easy positioning at the furnace opening **14**. Also provided is an air duct **16** that conducts cooling air to both the glass furnace opening and the furnace charger. Positioned atop the glass furnace charger **12** is the glass batch mixing apparatus **18** and positioned immediately adjacent such mixing apparatus is the batch delivery means **20**.

As is apparent, glass batch is delivered to the mixing apparatus **18** through the delivery means **20** and subsequent to being wetted and mixed, exits into the furnace charger hopper **22**. Thereafter, the batch is intermittently delivered to the furnace opening **14** by the pusher element or feeding means **24**. In effect, therefore, the mixing apparatus **18** becomes an extension of the charger hopper **22** and, as has been typical, glass batch that is delivered to the hopper moves therethrough basically as a result of gravity flow.

The glass batch mixing apparatus **18**, as can best be seen in Figure 1.1b, is composed of a receptacle **26** having a top inlet opening **28** and a bottom outlet opening **30** which will accommodate the gravity flow of glass batch through the receptacle **26**. Also, it should be noted that the wall construction of the receptacle **26** is designed such that the bottom outlet opening **30** is of approximately the same size as the inlet opening of the furnace charger hopper **22**. Accordingly, upon attachment of the mixing apparatus **18** to the furnace charger **12**, these respective openings **22, 30** are aligned and the mixing apparatus thereby effectively becomes an enlargement of the basic hopper construction **22** of furnace charger **12**.

The receptacle **26** has positioned therein a rotatably mounted mixing means **32** which is comprised of two main rotatable shafts **34**, each being driven through a suitable chain and sprocket assembly **36**, and gear reducer **40** by motor **38**. Also positioned within the receptacle **26** is a deflection baffle **42** which is adapted to redirect glass batch as it is delivered from delivery means **20** to a position above each of the mixing means **32**.

It is preferred that the sprocket assemblies **36** be of the type that incorporates a slip clutch arrangement. Such arrangement will minimize the possibility of damaging the various driving means **36, 38, 40** in the event of the mixer jamming or plugging.

Similarly, there is affixed to the receptacle **26** a fluid delivery system **44**, comprised of fluid conduits **46** and delivery means **48**, the latter being typical full cone fluid spray nozzles. These nozzles **48** are similarly positioned above the deflection baffle **42** and adjacent to the batch delivery means **20** so that as batch is delivered therefrom, it may be fully wetted in the preparation for mixing and passage through the receptacle **26**.

Full cone nozzles **48**, as opposed to hollow cone or flat spray nozzles, are preferred because such tend to provide the most uniform wetness to the surface of the batch upon its initially entering the mixer **18**.

The driving means **36, 38, 40** is adapted for constant operation so that the rotatably mounted mixing means **32** within the receptacle **26** is in constant motion, thereby agitating the glass batch within that receptacle even in the absence of batch movement through same.

The particulate materials in the noted receptacle accordingly are not afforded any opportunity to cake or otherwise solidify because of their wetted condition. The speed of rotation will, of course, be determined by the batch consistency, its speed of movement through the receptacle and the degree of wetness of the batch itself. Accordingly, such will be subject to experimentation and adjustment based upon operating conditions that may be encountered in any particular situation.

Each of the rotatably mounted mixing means **32** incorporates upon shaft **34**, agitating means **50** which is composed of radically protruding paddle members **52** affixed to pins **54**. Each of the shafts **34** is suitably bored to accept the pins **54**. These bore holes are positioned along and around the shafts in a symmetrical relationship that provides for a slight overlap of the area swept by paddle members **52** during shaft rotation and at approximately a 90° offset with respect to each adjacent bore hole. The agitating means **50** is affixed to the shafts **34** as is shown.

Melting Apparatus Using Gas-Free Materials

E.T. Strickland; U.S. Patent 4,138,238; February 6, 1979 describes a method of melting glass-forming materials comprising:

(a) Establishing a bed of particulate substantially gas-free, glass-forming materials;

(b) Urging the particulate materials into close proximity with a resistance heating member, the heating member having at least one outlet for molten glass;

(c) Melting the glass-forming materials with heat transmitted from the resistance heating member to form molten glass;

(d) Maintaining only a thin film of molten glass on the heating member;

(e) Flowing the molten glass through the outlet; and

(f) Collecting the molten glass in a heated reservoir having a gas space over the molten glass.

Unlike the common prior art glass melting processing, the raw materials for this process should be substantially gas-free. Most raw materials can be readily rendered substantially gas-free merely by preheating or calcining. Calcination temperatures are well-known to the art. The raw materials are substantially gas-free in order to avoid a rapid and unmanageable generation of gas during melting.

In the process, the charge moves toward the melter essentially as a unified body. Excessive gas formation at or near the melter can disrupt the integrity of the batch and can greatly reduce the efficiency of the melting process. Small amounts of gas, including the gas in the interstices between the particles of the charge, can be tolerated without disrupting the process. The resistance heater should achieve a temperature of at least about 2600°F, with temperatures of from about 2900° to 3100°F being particularly preferred.

In Figure 1.2a, the apparatus **10** includes a hopper **2** overlying and in communication with resistance heater **1**. The resistance heater is supported by ceramic supporting means **5** and overlies heated reservoir **6**.