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# INFORMATION PROFILES ON POTENTIAL OCCUPATIONAL HAZARDS

## VOLUME III. INDUSTRIAL PROCESSES

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Abstract (Limit: 200 words)

ABSTRACT: This information profile on glass and ceramics manufacture (SIC-32) is part of a group of 46 such profiles that provide information about chemicals or industrial processes considered to be potential occupational hazards. Each profile contains summary data on known and suspected health effects, the extent of worker exposure and the industrial importance of either a single chemical, class of chemicals, or a particular industrial process. The report was developed for use by occupational safety and health professionals in industry, and labor and other areas, to provide them with a synopsis of information in their workplaces.

Document Analysis a. Descriptors

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## INTRODUCTION

An information profile is a working paper used by the National Institute for Occupational Safety and Health (NIOSH) to assist in establishing Institute priorities. It is an initial step in determining the need to develop comprehensive documents or to initiate research. Each profile summarizes data on known and suspected health effects, the extent of worker exposure, physical and chemical properties, and the industrial importance of individual chemicals and classes of chemicals. The profile may also be used by industry, labor, and the occupational health community as a synopsis of information on each subject and to identify possible health hazards associated with their workplaces.

Although detailed literature searches are conducted using computerized and manual searching techniques to identify pertinent and recent information, not all the literature obtained is incorporated in the report due to the summary nature of the profiles. Further, literature published after 1978 may not be included in these profiles because it was generally unavailable at the time the search was completed.

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GLASS AND CERAMICS MANUFACTURING

## I. SCOPE OF PROFILE

The processes used to manufacture glass and ceramic products have been reviewed for the purpose of identifying the potential occupational health hazards associated with the glass and ceramic industries.

The subject industries are engaged in manufacturing various forms of glass products, ceramic tile products, vitreous china ware, food utensils, plumbing fixtures, refractories, and other pottery products from silicous, carbonaceous, argillaceous, and feldsparic sands, sediments, and stone. Establishments involved in the manufacture of glass and clay products are categorized by the Standard Industrial Classification (SIC) manual as follows:

SIC 3211 - Flat glass
SIC 3221 - Glass containers
SIC 3229 - Pressed and blown glass
SIC 3231 - Glass products made of purchased glass
SIC 3251 - Brick and structural clay tile
SIC 3253 - Ceramic wall and floor tile
SIC 3255 - Clay refractories
SIC 3259 - Structural clay products, not elsewhere classified (n.e.c.)
SIC 3261 - Vitreous plumbing fixtures
SIC 3262 - Vitreous china food utensils
SIC 3263 - Fine earthenware food utensils
SIC 3264 - Procelain electrical supplies
SIC 3269 - Pottery products, not elesewhere classified (n.e.c.)

Complete descriptions of these categories are presented in Appendix A.

## II. SUMMARY

Glass manufacture basically involves melting a dry feed mixture (containing glass sand, soda ash, limestone, and feldspar for soda lime glasses) and subsequent forming into finished shapes by pressing, blowing, casting, rolling, drawing, annealing, or other finishing operations. Ceramic production first involves crushing, grinding, and pulverizing raw clay feed materials (typically hydrated silicates of aluminun, iron, or magnesium), and subsequent shaping by various forming processes such as extrusion, soft plastic forming, dry pressing, and slip casting. After shape forming, the products are fired for strength.

Adverse health effects may result from airborne siliceous dusts generated during the preparation of glass and ceramic feed mixtures, emissions associated with melting, burning, and drying operations, and high temperature exposures at the glass melting tanks, pottery kilns, and clay firing furnaces. In addition, the manufacture of pottery and related ceramic products may involve exposure to potentially toxic glazing compounds.

## III. STATISTICAL INFORMATION

In 1976, 223,000 production workers were employed in 2852 glass and ceramic establishments (Anon., 1978a). The distribution of these totals among the several processes and the number, sizes, and types of establishments are detailed in Table 1. In 1976, about 65% of the total number of workers were employed in the glass plants. Over 60% of the glass plants were engaged in manufacturing products from purchased glass (SIC 3231); nearly 85% of these plants employed less than 50 production workers.

Incidence rates of occupational injuries and illnesses in glass and ceramic operations are presented in Table 2. As indicated in Table 2 and detailed below, the injury and illness rates for the several major divisions of the industry exceed the average rate for all manufacturing in the U.S. in 1977 (13.1 cases/100 employed):

| | |
|---|---|
| Glass manufacture (SIC 321, 322, 323) | = 18.5 cases/100 employed |
| Clay product processes (SIC 325) | = 18.1 cases/100 employed |
| Pottery product processes (SIC 326) | = 16.4 cases/100 employed |

Table 1. Glass and Ceramic Industries (Employment Information)[a]

1976

| SIC | Process | Number of Establishments | Number of Production Workers[b] (in thousands) | Average Number of Production Workers per Establishments | Number of Establishments by Number of Employees: 1 to 4 | 4 to 9 | 10 to 19 | 20 to 49 | 50 to 99 | 100 to 249 | 250 to 500 | Over 500 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3211 | Flat glass | 92 | 18 | 195 | 27 | 14 | 10 | 11 | 1 | 3 | 9 | 17 |
| 3221 | Glass containers | 121 | 63 | 520 | 1 | 1 | 0 | 3 | 0 | 14 | 49 | 53 |
| 3229 | Pressed and blown glass | 233 | 37 | 115 | 25 | 41 | 34 | 23 | 19 | 30 | 21 | 40 |
| 3231 | Products from purchased glass | 880 | 27 | 31 | 329 | 152 | 122 | 139 | 62 | 50 | 16 | 10 |
| | Total for Glass Industry | 1326 | 145 | | 382 | 208 | 166 | 176 | 82 | 97 | 95 | 120 |
| 3251 | Brick and structural clay | 339 | 17 | 50 | 34 | 23 | 44 | 107 | 86 | 40 | 5 | -- |
| 3253 | Ceramic wall and floor tile | 73 | 7 | 95 | 18 | 5 | 5 | 11 | 9 | 18 | 5 | 2 |
| 3255 | Clay refractories | 167 | 9 | 55 | 21 | 14 | 17 | 46 | 39 | 20 | 7 | 3 |
| 3259 | Structural clay products n.e.c. | 99 | 5 | 50 | 19 | 8 | 14 | 22 | 17 | 16 | 3 | -- |
| | Total for Clay Industry | 678 | 38 | | 92 | 50 | 80 | 186 | 151 | 94 | 20 | 5 |
| 3261 | Vitreous plumbing fixtures | 62 | 8 | 130 | 13 | 4 | 7 | 4 | 7 | 15 | 8 | 4 |
| 3262 | Vitreous china food utensils | 32 | 5 | 156 | 5 | 3 | 3 | 5 | 5 | 3 | 4 | 4 |
| 3263 | Fine earthenware food utensils | 18 | 6 | 330 | 3 | -- | 2 | 1 | 2 | 4 | 1 | 5 |
| 3264 | Porcelain electrical supplies | 74 | 9 | 120 | 9 | 4 | 11 | 11 | 9 | 21 | 3 | 6 |
| 3269 | Pottery products n.e.c. | 562 | 12 | 22 | 305 | 88 | 63 | 51 | 28 | 20 | 5 | 2 |
| | Total for Pottery Industry | 748 | 40 | | 335 | 99 | 86 | 72 | 51 | 63 | 21 | 21 |
| | Total for all Glass and Ceramic Industries | 2842 | 223 | | 809 | 357 | 332 | 434 | 284 | 254 | 136 | 146 |

[a] Anon., 1978b except as noted
[b] Anon., 1978a

Table 2. Glass and Ceramic Industries (Incidence Rates for Injuries and Illness) (Anon., 1979)

1977

| SIC | Process | Incidence Rates per 100 Full-Time Workers: Injury and Illness (Per 100 employed) Total cases | Injury and Illness Lost work days | Injury (Per 100 employed) Total cases | Injury Lost work days | Illness (Per 100 employed) Total cases | Illness Lost work days | Lost work day cases |
|---|---|---|---|---|---|---|---|---|
| | All manufacturing average | 13.1 | 82.3 | 12.6 | 79.3 | 0.5 | 3.0 | 4.8 |
| 32 | Stone, clay and glass products | 16.9 | 120.4 | 16.3 | 116.0 | 0.6 | 4.4 | 6.9 |
| 321 | Flat glass | 19.4 | 98.1 | 19.3 | 96.3 | 0.1 | 1.8 | 4.9 |
| 322 | Glass and glassware | 15.0 | 136.2 | 14.2 | 125.3 | 0.8 | 10.0 | 6.8 |
| 323 | Products from purchased glass | 19.9 | 140. | 19.1 | 99.8 | 0.8 | 4.2 | 6.7 |
| 325 | Structural clay products | 18.1 | 134.1 | 17.8 | 131.4 | 0.3 | 2.7 | 8.2 |
| 3251 | Brick and structural tile | 20.7 | 149.1 | 20.4 | 146.0 | 0.3 | 3.1 | 9.2 |
| 3253 | Ceramic wall and floor tile | 12.6 | 90.2 | 12.2 | 88.5 | 0.4 | 1.7 | 5.3 |
| 3255 | Clay refractories | 14.7 | 113.0 | 14.3 | 111.6 | 0.4 | 1.4 | 0.6 |
| 3259 | Other structural clay products n.e.c. | 24.4 | 189.2 | 24.1 | 186.4 | 0.3 | 2.8 | 12.7 |
| 326 | Pottery and related products | 16.4 | 114.8 | 15.6 | 109.2 | 0.8 | 5.6 | 7.9 |
| 3261 | Vitreous plumbing fixtures | 25.6 | 185.6 | 24.6 | 180.4 | 1.0 | 8.1 | 13.5 |
| 3262 | Vitreous china food utensils | 8.3 | 128.6 | 7.5 | 124.5 | 0.9 | 4.1 | 5.7 |
| 3263 | Fine earthenware food utensils | 13.6 | 108.7 | 13.0 | 99.1 | 0.6 | 8.6 | 7.7 |
| 3264 | Porcelain electric supplies | 12.2 | 99.9 | 11.7 | 93.1 | 0.5 | 6.8 | 5.3 |
| 3269 | Other pottery products | 13.8 | 70.2 | 13.2 | 69.0 | 0.6 | 1.2 | 5.1 |

The following tabulation presents the five sections of the glass and ceramics that have particularly high rates for injuries and illnesses and, thus, are the principal contributors to the high group rates.

| SIC | Process | Rate[a] Total cases per 100 workers | Production workers (1000)[b] | Number of Establish-ments[c] |
|---|---|---|---|---|
| 3261 | Vitreous Plumbing Fixtures | 25.6 | 7.7 | 62 |
| 3259 | Structural Clay Products | 24.5 | 5.0 | 99 |
| 3251 | Brick and Structural Tile | 20.7 | 17.0 | 339 |
| 3231 | Products from Purchased Glass | 19.9 | 27.0 | 880 |
| 3211 | Flat Glass | 19.4 | 18.0 | 92 |

[a] Anon., 1979
[b] Anon., 1978a
[c] Anon., 1978b

The remaining operations averaged 13.3 cases/100 workers.

## IV. PRODUCTION AND TRENDS

Glass, structural clay, and pottery products had a total sales value of $10,900 million in 1976 (Anon., 1978a). Other production data, including annual growth in employment and plant locations, are summarized in Table 3.

## V. CHARACTERIZATION OF PROCESSES

### A. Glass Manufacture (SIC 321, 322 and 323)

Ninety percent of all glass is a soda-lime product having the following typical composition (Hutchins and Harrington, 1966):

| | |
|---|---|
| $SiO_2$ | 72% |
| $Na_2O$ | 15% |
| $CaO + MgO$ | 10% |
| $Al_2O_3$ | 2% |
| Other | 1% |
| | 100% |

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Table 3. Glass and Ceramic Industries (Annual Sales, Growth and Plant Locations)[a]

1976

| SIC No. | Process | Value of Shipments | Establishments[b] | Employees: All | Employees: Production Workers | Annual Growth in Employment* | Locations**: New England | Mid Atlantic | East North Central | West North Central | South | West |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | ($ million) | (Number) | (1000) | (1000) | % | % | % | % | % | % | % |
| 32 | Stone, clay and glass products | 30,635 | 15,713 | 599 | 474 | <-1 | 5 | 15 | 22 | 10 | 30 | 18 |
| 3211 | Flat glass | 1,336 | 92 | 22 | 18 | +1 | 3 | 13 | 28 | 6 | 40 | 10 |
| 3221 | Glass containers | 3,300 | 121 | 71 | 63 | <-1 | 3 | 25 | 23 | 5 | 32 | 12 |
| 3229 | Pressed and blown glass | 1,855 | 323 | 44 | 37 | <-1 | -- | -- | -- | -- | -- | -- |
| 3231 | Products of purchased glass | 1,651 | 880 | 35 | 27 | <+1 | 3 | 35 | 21 | 4 | 18 | 17 |
| | Total for Glass Industry | 8,142 | 1,416 | 172 | 145 | | | | | | | |
| 325 | Structural clay products | 1,595 | 688 | 47 | 38 | -2 | 3 | 16 | 20 | 9 | 35 | 17 |
| 326 | Pottery and related products | 1,165 | 748 | 45 | 40 | ±0 | 6 | 20 | 18 | 5 | 24 | 28 |
| | Total for Clay and Pottery Industries | 2,760 | 1,436 | 92 | 78 | | | | | | | |
| | Total for Glass, Clay, and Pottery Industries | 10,902 | 2,852 | 264 | 228 | | | | | | | |

[a]Anon., 1978a except as noted
[b]Anon., 1978c
*(1972-1976)
**Approximated from 1972 census data (Anon. 1975)

In other compositions such as borosilicate, aluminosilicate, and lead glasses, the indicated additions are used to produce specific properties, e.g., heat and thermal shock resistance, or electrical or optical properties.

In all cases, initial processing involves melting the dry feed mixture. This contains glass sand, soda ash, limestone and feldspar for soda lime glasses. These materials are usually received in bags or bulk, and are batch mixed with recycled crushed cullet and charged into an oil or gas fired continuous reverberatory tank type furnace. The charge is heated to nearly 1500°C and subsequently passed to a cooling and discharge section held at about 1300°C, allowing it to degas. The melt is finally discharged at 800-1100°C before forming into finished shapes by pressing, blowing, drawing, or rolling. These shapes are then annealed at approximately 1500°C for 60-90 minutes in a continuous belt tunnel lehr. Final steps include product finishing, inspecting, packing, and shipping.

The furnaces are provided with checkerwork regenerators for heat conservation. Dusting of the dry charge is a persistent problem. Small amounts of water are commonly sprayed on the feed mix to minimize the dust which is carried into the regenerator checkerwork. Briquetting the feed mix is also used to reduce dusts in some plants.

The furnaces are charged manually or mechanically with screws or pusher feeders, usually in 1000-3000 pound batches. The furnaces are lined with high alumina refractory brick and contain a bridge-wall that separates the melting zone from the discharge sections.

The furnaces range in holding capacity from a few tons to 1500 tons depending on the product and the capacity of the plant. Production capacities range from a few tons up to 3000 tons per day. Furnace dimensions may approach 150 feet in length and 30 feet in width; depths vary from 3 to 15 feet. The combustion gases pass from the regenerators to flue systems and stacks.

The forming operations involve the following processes (Hutchins and Harrington, 1966; Scholes, 1975):

Pressing - The objects are formed in molds that are fitted with plungers that press the charge into shape. The products, which are usually less than 12 inches in diameter and 4 inches in height, weigh up to approximately 35 pounds; plunger pressures range up to 120 psi. The molds may be manually or automatically operated. The process is used for tableware and laboratory glass articles.

Blowing - Hand-blown glass is made with a blowpipe, often using lung power to develop internal pressures in melted "gobs" of glass. The object is shaped by blowing the gob after it is placed in a steel mold. For circular shaped products, the molds are lubricated with shellac, charcoal or linseed oil to facilitate rotating the product in the mold. The operation is also performed mechanically by feeding the blank molds with gobs of glass, spreading with compressed air, and subsequently preforming with a counterflow of air. The preformed articles are transferred to blow molds for finishing into desired shapes. The method is used for forming bottles and is adapted by "ribbon machines" to make incandescent lamp envelopes, bulbs, etc. Up to 2200 bulbs per minute are produced by ribbon machines.

Casting - Casting consists of pouring the melt into molds, or onto tables or rolls to form the products. Centrifugal casting is also used; in this method, the glass gobs are dropped into a spinning mold that shapes the object by centrifugal force.

Rolling - Essentially all flat glass is manufactured by the float process. This process consists of passing molten glass from a continuous melting tank forehearth through a rolling machine and, while soft, onto a bath of molten tin alloy in an oxygen-free chamber. The smooth 10 to 12 feet wide product is discharged through an annealing lehr and cut to size for packing and shipping. The float process has completely replaced the old plate glass process; this process consisted of pouring a batch of molten glass onto a large iron table, rolling to the desired thickness with an iron roller, and subsequent grinding and polishing.

Drawing - Several drawing processes are employed for the manufacture of tubing, sheet, and rods. Tubing is made by drawing the molten glass over a refractory mandrel in which air is blown to develop the tubular shape. Tubing is also made by drawing the melt through a die with a central plug. Sheet glass is drawn vertically through a slotted floating clay block, or over a submerged bar. The sheet is passed over cooling rolls and finally through an annealing lehr. No grinding or polishing is usually required.

Annealing - Annealing is carefully controlled to give the desired properties to the products. The main objective is to relieve stresses developed during solidification. Cooling is held in a range of temperature above the strain point, which depends on the viscosity of the melt.

Finishing - Other finishing operations are flame cutting, sawing, score breaking, drilling, and grinding. Carbide and diamond are used as the abrasive for blades, files, wheels, and drills. Sand, garnet, corundum, silicon and boron carbide, and diamond are used for grinding. Polishing uses cerium, zirconium, and ferric oxides.

Dilute hydrofluoric acid is used for acid etching such as the inside of lamp bulbs. Glazing to color, decorate, or improve physical properties consists of firing the product at a temperature that will melt the glaze, but not deform the glass base. The glaze is first applied in a suspension of the glaze-forming constituents. Vitrifiable enamels are applied directly. The latter include metals and a wide variety of oxides that have been mixed with glass frits for manual application and firing.

Secondary forming is used to improve dimension tolerance for specific applications. Other secondary operations include coating with metals, and product foaming, tempering, staining, and sintering for special applications. Production of laminated automobile safety glass is an important secondary operation. This consists of laminating two 0.125-inch thick sheets of glass with a 0.015 inch sheet of polyvinyl butyral. The operation involves stacking the sheets together and degassing in oil at about 140°C and 200 psi. The glass is "sagged" into shape by heating with weights to about 580°C.

## B. Manufacture of Structural Clay and Other Ceramic Products (SIC 325 and SIC 326)

Clay is a sedimentary material formed and deposited in nature by the action of water and carbon dioxide in feldspar pegmatites. The predominant components of clay minerals are hydrated silicates of aluminum, iron, or magnesium. The principal clay minerals are kaolinite [$Al_4Si_4O_{10}(OH)_8$] and other similar aluminosilicate compositions ranging from approximately 26-40% $Al_2O_3$ and 45-60% $SiO_2$ (Hamme, 1979).

The clays used in the pottery and in structural clay products range from pure kaolinite-type minerals containing 35-40% $Al_2O_3$ (Norton, 1970),



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through lower purity kaolins, to low purity clay materials such as brick and tile clays. Plasticity and other shape-forming and shape-holding properties of the blends, the strength of the preformed green product shapes, and, ultimately, the strength of the products when fired or treated thermally are influenced by clay content.

The principal clays are classified as follows with respect to purity, plasticity, color, and softening temperatures (Hamme, 1979):

Kaolins are the highest purity and the most refractory clays. They have softening temperatures in the range of 1700-1750°C, and are used for whiteware bodies and refractories. Kalonite is the most common highest quality kaolin.

Ball Clays are less pure kaolins with high plasticity, and are used for slips and enamels, and some whiteware, sanitary, and tile products.

Fire Clays have fusion temperatures above 1500°C, and are used for fire clay brick, glass melting pots, linings, crucibles, refractory cements, and nonplastic grogs.

China Clays are white-firing kaolins used for the manufacture of china and similar whitewares.

Slip Clays are impure clay forms, with low softening points, used for glazing.

Bentonite is a highly plastic clay, used to increase the plasticity and the strength of prefired bodies.

Pottery Clays are commonly used for making earthenware and stoneware products such as flower pots.

Sewer Pipe Clays are approximately the same as pottery clays.

Brick Clays include a wide variety of clays, usually plastic, and are selected for fired color.

The principal nonclay minerals used in the various process blends are as follows:

*Quartz, sandstones, and sand* as sources of silica for brick, whiteware bodies, and enamels.

*Feldspars*, for use as fluxes, especially in whiteware bodies, as a source of alkali.

*Limestone*, for a source of calcium.

*Miscellaneous Minerals*, additives for mortars and specific properties (Hamme, 1964).

New ceramics include so-called pure oxide ceramics for many special electrical and refractory uses. These include oxides such as alumina, zirconia, thoria, beryllia, magnesia, and mineral complexes (Kingery *et al*., 1976).

### Forming Processes

In preparing to form ceramic products into desired shapes, it is necessary to pulverize raw feed material particles to a fineness that allows thorough mixing. The operation consists of a series of crushing, grinding, and pulverizing steps with screens or air classifiers to control the sizing. Jaw crushers, hammer mills, rolls, and rod and pebble mills are used, either for batch or continuous operation. The operation may be wet or dry, depending on the materials and the product. The wet process lessens the dustiness and improves the granulation, but usually requires filtration and drying of the mixture (Stoop, 1979).

Mixing is also usually required. Drum type mixers are used for dry feed, and blungers are used for wet mixing. Magnetic separation may be necessary to remove iron, especially for whiteware.

Cold-forming processes at normal temperatures are the most common methods used for shaping the product for firing, although the use of hot-forming processes is increasing.

Ceramic forming processes, as compiled from Norton (1970), Grimshaw (1971), and Stoop (1979) include:

Extrusion involves feeding the mixture into the feed box of a pug mill where it is stirred and some water incorporated into the mixture. From here, it is fed through a de-aerating screw auger in a vacuum box. This is followed by a high pressure auger that extrudes the mix through a die of the desired cross section, after which it is cut into bricks. Extrusion is widely used for structural clay products and to a lesser extent for fine pottery.

Soft plastic forming requires that the mix contain sufficient plastic clay and water to form with only a little pressure. Extruded slugs of the mix are fed onto revolving molds where the product is formed by contours in the mold and by spinning action or jiggering. Hand molding by tamping or ramming the clay into shape also requires the use of soft plastic clays. Soft plastic forming processes are most widely used for dinnerware, chemical porcelain, and electric insulators, as well as for products with especially intricate shapes.

Dry pressing, in which partially dried feed mix is formed by pressing through the cavity of a die with pressures of 5,000 to 30,000 psi, is used extensively for the manufacture of simple shapes of whitewares, refractories, and abrasives in large quantities. Vibratory, impact, and isostatic forming modifications are used to obtain uniform pressure conditions.

*Slip casting* consists of pouring suspensions of the clay mixtures (slip) into porous plaster molds. The external surface of the ware is formed by the mold surface as the water from the slip is absorbed by the plaster. Intricate shapes are formed by this method, especially plumbing ware and some dinnerware. Nonplastic materials such as refractory oxides and carbides may be formed by slip casting (Hackler, 1964; Stoop, 1979).

### *Thermal Treatment*

Ceramic products require thermal treatment by firing at temperatures from about 700°C for enamels to 1650°C or more for alumina ceramics. A wide variety of furnaces are used (Hackler, 1964; Norton, 1971; Jones and Berard, 1972; Hare, 1979).

*Tunnel kilns*, as commonly used, are designed so that flat cars with refractory tops and understructures protected from the kiln gases convey the ware through zones with progressively increasing temperature. Gas, oil, or electric resistance units supply the heated gases. After the high temperature zone, the ware is moved through a cooling zone, into which air is blown at controlled rates. Tunnel kilns range from 75 to 500 feet in length, 2 to 10 feet wide and 4 to 10 feet high. Practically all grades of clay products, tile, porcelain, dinnerware, and refractories are fired in tunnel kilns.

*Arc melting* is used to melt such materials as alumina, magnesia, and mullite before casting into pigs. The process is used to remove impurities by an evaporation action. This process, fusion casting, is used in producing refractory linings for high temperature furnaces.

*Hot pressing* combines forming and firing in one operation. The feed is placed in graphite dies and heated by induction while pressure is applied. The process gives a dense product.

Time and temperature are the principal variables that are controlled in firing ceramic products. Thermocouples, radiation, and optical pyrometers are usual instruments for temperature measurement. Pyrometric cones are also used to integrate temperature with time and mix composition.

Furnace atmosphere is also controlled. Oxidizing conditions are usually held to avoid changes to the ceramic oxides. Neutral or reducing atmospheres may be used for special treatment for color, conductivity, or magnetic properties. Nitrogen atmospheres and vacuum conditions may be used, especially for extreme temperature firing.

Porous ceramics are formed by mixing organic materials, which burn out during firing, into the feed, or by underfiring a regular composition of graded particles.

Colors and glazes are applied to pottery, as to glass, by applying a mix of the desired materials including fluxes such as lithium compounds, and frits, and firing to a temperature that does not soften the base.

## VI. ENGINEERING CONTROLS

Information on specific design features of glass and ceramic manufacturing facilities is generally proprietary, and unavailable from published literature sources.

The generation of airborne siliceous dusts, and emissions associated with melting, burning, drying, and glazing operations can be controlled by properly designed, operated, maintained, and monitored ventilating systems.

Automatic controls and measurements may reduce exposures to high temperature blow-backs and other adverse temperature conditions.

## VII. POTENTIAL HEALTH HAZARDS

The most persistent potential hazards associated with glass and ceramic manufacturing operations are airborne siliceous dusts that are generated from the preparation of unfired feed mixes, and high process temperatures (e.g., exposures at glass melting tanks, pottery kilns, and clay firing operations) (Section V). The manufacture of pottery and related products may also involve exposure to numerous potentially toxic glazing compounds. A listing of some of the potentially hazardous chemicals associated with the manufacturing processes and a summary of their uses and health hazards are presented in Table 4 (NIOSH, 1977b; Proctor and Hughes, 1978). It should be emphasized, however, that this presentation is intended merely to identify some of the major health problems, and is neither comprehensive nor critical.

Prowse and Cavanagh (1976) surveyed the occurrence of tuberculosis in North Staffordshire, England during the period 1971-1974 by collecting and examining records of notification of tuberculosis. Notification rates for North Staffordshire were compared with figures for England, Wales, and Birmingham and it was observed that the number of notified cases of tuberculosis had risen in this region. The proportion of notifications in the small immigrant community of this stable population did not account for the rise in notification rates for the region. High notification rates were found in mining and pottery workers. As indicated in Table 5, the notification rates for male and female workers in the pottery industry were almost twice those of the general population; the incidence may even be higher because many cases occurred in retired workers but were not included in the figures. The incidence of tuberculosis was unrelated to either the presence of pneumoconiosis or the age of the patient; however, the number of cases was small. Prowse and Cavanagh also noted the occurrence of 57 cases of disability pensions given for

Table 4. Chemical Hazards Associated with the Glass and Ceramics Industries NIOSH, 1977b; Proctor and Hughes, 1978)

| | | Routes of Entry | | | Harmful Effects | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Animal | | | Human | | |
| Material | Principal Use | Inhl. | Dermal | Oral | Local | Systemic | Carcinogen | Local | Systemic | Carcinogen |
| Arsenic | Bronzing, decolorizing agent; used in manufacture of opal glass and enamels | x | x | x | x | x | | x | x | x |
| Antimony and compounds | Used in manufacture of lacquers, glass, pottery, enamels and glazes | x | x | x | | | | x | x | |
| Fluorocarbons | Used by ceramic mold makers | x | | | | | | x | x | |
| Acetylene | Flame used in glass industry | x | | | | | | | x | |
| Oxalic acid | Used in ceramic manufacture | x | | | | | | x | x | |
| Fluorine and compounds | Fluoride exposure may also occur from kiln firing of brick & ceramic materials, and from the melting of raw materials in glassmaking. Hydrogen fluoride used in removing effervescence from bricks and stones; and in frosting and etching glass and enamel. Fluorides are used in manufacture of glass, ceramics, pottery, enamels, and glassware. | x | | x | x | x | | x | x | |



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Table 4. Chemical Hazards Associated with the Glass and Ceramics Industries (NIOSH, 1977b; Proctor and Hughes, 1978) (Cont'd)

| | | Routes of Entry | | | Harmful Effects | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Animal | | | Human | | |
| Material | Principal Use | Ihl. | Dermal | Oral | Local | Systemic | Carcinogen | Local | Systemic | Carcinogen |
| Barium and compounds | Used in tile manufacture, glazes, and glassmaking | x | | x | | | | x | x | |
| Beryllium and compounds | Used in manufacture of ceramics and refractories | x | | | x | x | | x | x | |
| Cobalt and compounds | Pigments in enamels, glazes and in glass and pottery industry | x | | | | | | x | x | |
| Lead-Inorganic | Used in vitreous enamelling, ceramic glazes. Ingredients in glass and pigments. | x | | x | | x | | | x | x |
| Uranium and compounds | Used in staining glass, glazing ceramics and enamelling. | x | x | | x | x | x | x | x | x |
| Vanadium and compounds | $V_2O_5$ is used in glass and ceramic glazes | x | | | | | | x | x | |
| Zirconium and compounds | $ZrSiO_2$ used as an opacifier for glazes and enamels and in frittered glass filters. Others used in enamels, white glass, refractory crucibles and ceramics. | x | | | | x | | x | | |

Table 4. Chemical Hazards Associated with the Glass and Ceramics Industries NIOSH, 1977b; Proctor and Hughes, 1978) (Cont'd)

| | | Routes of Entry | | | Harmful Effects | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Animal | | | Human | | |
| Material | Principal Use | Ihl. | Dermal | Oral | Local | Sys-temic | Carcino-gen | Local | Sys-temic | Carcino-gen |
| Picric acid | Manufacture of colored glass | x | x | x | x | x | | x | x | |
| Thallium and compounds | Manufacture of optical lenses, glassware | x | x | x | | | | x | x | |
| Cerium and compounds | Opacificer in certain metals; used in manufacture of topaz yellow glass incandescent gas mantels and in de-colorizing glass. | x | | | | x | | | | |
| Boron and compounds | Boric acid used in manufacture of glass, pottery, enamels, glazes, cements, and porcelain, borax is used in the manufacture of enamels and glazes. | x | | x | x | x | x | x | x | |
| Chromium and compounds | Used in manufacture of glass | x | x | x | | | | x | x | x |
| Germanium | Used in production of optical glass & lenses | x | | | | | | x | x | |
| Sulfur dioxide | Used in manufacture of glass | x | x | | x | x | x co-car | x | x | |

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Table 4. Chemical Hazards Associated with the Glass and Ceramics Industries (NIOSH, 1977b; Proctor and Hughes, 1978) (Cont'd)

| | | Routes of Entry | | | Harmful Effects | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Animal | | | Human | | |
| Material | Principal Use | Ihl. | Dermal | Oral | Local | Systemic | Carcinogen | Local | Systemic | Carcinogen |
| Manganese and compounds | Decolorizer and coloring agent in glass and ceramics industry | x | x | | | | | x | x | |
| Molybdenum and compounds | Electrodes for glass melting; coating for quartz glass. Decorating ceramics. | x | | | | x | | x | | |
| Nickel and compounds | Used in manufacture of ground-coat enamels, colored ceramics, and glass. | x | | | | | x | x | x | x |
| Silica | Ingredient of ceramic bodies and glazes, used in making structural and firebrick, other refractories, glass. | x | | | x | x | | x | x | |
| Silver and compounds | Application of metallic films on glass and ceramics. Compounds are used in coloring glass and ceramics. | x | | x | x | x | | x | x | |
| Tellurium and compounds | Coloring agent in glazes and glass | x | x | | | x | | x | x | |
| Thorium and compounds | Used in ceramics. | x | x | x | | | | x | x | x |

Table 5. Notification Rates for Tuberculosis Related to Occupation in the Potteries 1973-74 (Prowse and Cavanagh, 1976)

| | Population | Cases | | Notification rate/$10^5$ | |
|---|---|---|---|---|---|
| | | 1973 | 1974 | 1973 | 1974 |
| Miners | 8,061 | 7 | 4 | 86.8 | 49.6 |
| Pottery industry workers: | | | | | |
| Males | 18,978 | 11 | 8 | 58.0 | 42.2 |
| Females | 22,510 | 3 | 10 | 13.3 | 44.4 |
| Both sexes | 41,488 | 14 | 18 | 33.7 | 43.4 |
| General population* | | | | | |
| Males (15-65 yr) | 122,261 | 32 | 29 | 26.2 | 23.7 |
| Females (15-65 yr) | 125,995 | 23 | 24 | 18.3 | 19.1 |
| Both sexes | 248,256 | 55 | 53 | 22.2 | 21.4 |

*excluding those working in the mining and pottery industries.



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pneumonoconiosis, out of 545 cases (333 males, 212 females) studied for evidence of other associated factors and diseases.

In an attempt to correlate rates of lung cancer to occupation, Menck and Henderson (1976) reviewed 2,161 death certificates mentioning lung cancer for 1968-70 and 1,717 cases of lung cancer in Los Angeles County for 1972-73. The Standard Mortality Ratio (SMR) was calculated according to the following formula: ratio of observed deaths plus incident cases to expected deaths plus incident cases; the SMR was 102 for white males 20-64 years of age, thus indicating no significant difference in this occupational group from the general population. General air pollution and smoking habits were not considered, thus limiting interpretation of the increased risk factor.

## VIII. PERTINENT NIOSH PUBLICATIONS

### A. Criteria Documents

| Subject | NIOSH Publication No. |
|---|---|
| Acetylene | 76-195 |
| Beryllium | 72-10268 |
| Chromium (VI) | 76-129 |
| Crystalline Silica | 75-120 |
| Hydrogen Fluoride | 76-143 |
| Inorganic Fluoride | 76-103 |
| Inorganic Lead | 73-11010 |
| Inorganic Nickel | 77-164 |
| Sulfur Dioxide | 74-111 |
| Vanadium | 77-222 |

### B. Health Hazard Evaluations (HHE's)

No health hazard evaluations of glass or ceramic manufacturing facilities were encountered.

### C. Other NIOSH Publications

No other relevant NIOSH publications were encountered.

## IX. EXISTING STANDARDS

A tabulation of ACGIH Threshold Limit Values (TLVs), OSHA promulgated standards, and NIOSH recommended criteria of chemical agents frequently encountered in glass and ceramics manufacturing operations is presented in Table 6.

## X. EXPOSURE ESTIMATES

As detailed in Section III, 223,000 production workers were employed in 2852 glass and ceramic manufacturing establishments in 1976 (Anon., 1978a).

## XI. ONGOING STUDIES

No relevant ongoing studies were identified.

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Table 6. Threshold Limit Values, OSHA Promulgated Standards, NIOSH Recommended Criteria*

| | ACGIH (ACGIH, 1977) | OSHA (OSHA, 1976) | NIOSH (NIOSH, 1977a) |
|---|---|---|---|
| Acetylene | Simple Asphyxiant | 2500 ppm (10% of lower explosive limit) | 2500 ppm (ceiling) |
| Antimony and Compounds** (as Sb) | 0.5 $mg/m^3$ | 0.5 $mg/m^3$ | 0.5 $mg/m^3$ |
| Arsenic and Compounds (as As) | 0.5 $mg/m^3$ | 0.5 $mg/m^3$ | 2 $\mu g/m^3$ (15-min ceiling) |
| Barium (soluble compounds) | 0.5 $mg/m^3$ | --- --- | --- --- |
| Beryllium | 0.002 $mg/m^3$ | 2 $\mu g/m^3$<br>5 $\mu g/m^3$ acceptable ceiling<br>25 $\mu g/m^3$ maximum ceiling/ (30-min) | 0.5 $\mu g/m^3$ (130-minute) |
| Cobalt metal, dust and fume** | 0.1 $mg/m^3$ | --- | --- |
| Fluorides, inorganic (as F) | 2.5 $mg/m^3$ | 2.5 $mg/m^3$ | 2.5 $mg/m^3$ |
| Fluorine | 2 $mg/m^3$ | --- | --- |
| Hydrogen Fluoride | 2 $mg/m^3$ | 3 ppm | 2.5 $mg/m^3$<br>5.0 $mg/m^3$ (15-min ceiling) |
| Lead, inorganic, fumes and dusts (as Pb) | 0.15 $mg/m^3$ | 0.2 $mg/m^3$ | <100 $\mu g/m^3$ |

*All values listed are 8-hr time-weighted average concentrations; except as indicated; NIOSH recommendations are based on up to a 10-hr exposure.

**Intended changes for 1977; Antimony, soluble salts (as Sb), 2 $mg/m^3$; Antimony trioxide, handling and use (as Sb), 0.5 $mg/m^3$. Cobalt metal, dust and fume (as Co), 0.05 $mg/m^3$.

Table 6. Threshold Limit Values, OSHA Promulgated Standards, NIOSH Recommended Criteria* (Cont'd)

| | ACGIH (ACGIH, 1977) | OSHA (OSHA, 1976) | NIOSH (NIOSH, 1977a) |
|---|---|---|---|
| Manganese and Compounds (as Mn) | 5 $mg/m^3$ (ceiling) | --- | --- |
| Molybdenum compounds (as Mo) | 5 $mg/m^3$ (soluble compounds)<br>10 $mg/m^3$ (insoluble compounds) | --- | --- |
| Nickel | 1 $mg/m^3$ (metal)<br>0.1 $mg/m^3$ (soluble compounds, as Ni) | 1 $mg/m^3$ (inorganic and compounds) | 15 $\mu g/m^3$ (inorganic and compounds) |
| Oxalic acid | 1 $mg/m^3$ | --- | --- |
| Picric acid | 0.1 $mg/m^3$ (skin) | --- | --- |
| Silica (crystalline quartz) | $\frac{10\ mg/m^3}{\%\ \text{Respirable quartz} + 2}$ (respirable dust)<br>$\frac{30\ mg/m^3}{\%\ \text{quartz} + 3}$ (total respirable and nonrespirable dust) | $\frac{10\ mg/m^3}{\%\ \text{Respirable quartz} + 2}$ | 50 $\mu g/m^3$ (respirable free quartz) |
| Silver, metal and soluble compounds, (as Ag) | 0.01 $mg/m^3$ | --- | --- |
| Sulfur dioxide | 5 ppm | 5 ppm | 0.5 ppm |



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Table 6. Threshold Limit Values, OSHA Promulgated Standards, NIOSH Recommended Criteria* (Cont'd)

| | ACGIH (ACGIH, 1977) | OSHA (OSHA, 1976) | NIOSH (NIOSH, 1977a) |
|---|---|---|---|
| Tellurium | 0.1 $mg/m^3$ | --- | --- |
| Thallium, soluble compounds (as Tl) | 0.1 $mg/m^3$ (skin) | --- | --- |
| Uranium (natural) soluble and insoluble compounds, (as U) | 0.2 $mg/m^3$ | --- | --- |
| Vanadium (as V) | 0.5 $mg/m^3$ ($V_2O_5$, dust)<br>0.05 $mg/m^3$ ($V_2O_5$, fume) | 0.5 $mg/m^3$ ($V_2O_5$ dust, ceiling)<br>0.1 $mg/m^3$ ($V_2O_5$ fume, ceiling) | 0.05 $mg/m^3$ (15-min ceiling) (vanadium compounds) |
| Zirconium Compounds (as Zr) | 5 $mg/m^3$ | | |

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APPENDIX A

(Anon. 1972)

# Major Group 32.—STONE, CLAY, GLASS, AND CONCRETE PRODUCTS

Group No. 322

*The Major Group as a Whole*

This major group includes establishments engaged in manufacturing flat glass and other glass products, cement, structural clay products, pottery, concrete and gypsum products, cut stone, abrasive and asbestos products, etc., from materials taken principally from the earth in the form of stone, clay, and sand. When separate reports are available for mines and quarries operated by manufacturing establishments classified in this major group, the mining and quarrying activities are classified in Division B. When separate reports are not available, the mining and quarrying activities other than those of Industry 3295 are classified herein with the manufacturing operations.

If separate reports are not available for crushing, grinding, and other preparation activities of Industry 3295, these establishments are classified in Division B.

Group No. Industry No.

**321** FLAT GLASS

**3211** **Flat Glass**

Establishments primarily engaged in manufacturing flat glass. This industry also produces laminated glass, but establishments primarily engaged in manufacturing laminated glass from purchased flat glass are classified in Industry 3231.

Building glass, flat
Cathedral glass
Float glass
Glass, colored: cathedral and antique
Glass, flat
Insulating glass, sealed units: *mitse*
Laminated glass, made from glass produced in the same establishment
Multiple-glazed insulating units, *mitse*
Opalescent flat glass
Ophthalmic glass, flat
Optical glass, flat
Picture glass
Plate glass blanks for optical or ophthalmic uses
Plate glass, polished and rough
Sheet glass
Sheet glass blanks for optical or ophthalmic uses
Skylight glass
Spectacle glass
Structural glass, flat
Tempered glass, *mitse*
Window glass, clear and colored

**322** GLASS AND GLASSWARE, PRESSED OR BLOWN

This group includes establishments primarily engaged in manufacturing glass and glassware, pressed, blown, or shaped from glass produced in the same establishment. Establishments primarily engaged in manufacturing glass products from purchased glass are classified in Industry 3231. 323

**3221** **Glass Containers**

Establishments primarily engaged in manufacturing glass containers for commercial packing and bottling, and for home canning.

Ampoules, glass
Bottles for packing, bottling, and canning: glass
Carboys, glass
Containers for packing, bottling, and canning: glass
Cosmetic jars, glass
Fruit jars, glass
Jars (packers' ware), glass
Jugs (packers' ware), glass
Medicine bottles, glass
Milk bottles, glass
Packers' ware (containers), glass
Vials, glass: made in glass making establishments
Water bottles, glass

Group No. | Industry No.

322 **GLASS AND GLASSWARE, PRESSED OR BLOWN—Continued**

**3229 Pressed and Blown Glass and Glassware, Not Elsewhere Classified**

Establishments primarily engaged in manufacturing glass and glassware, not elsewhere classified, pressed, blown, or shaped from glass produced in the same establishment. Establishments primarily engaged in manufacturing textile glass fibers are also included in this industry, but establishments primarily engaged in manufacturing glass wool insulation products are classified in Industry 3296. Establishments primarily engaged in the production of pressed lenses for vehicular lighting, beacons, and lanterns are also included in this industry, but establishments primarily engaged in the production of optical lenses are classified in Industry 3832. Establishments primarily engaged in manufacturing glass containers are classified in Industry 3221, and complete electric light bulbs in Industry 3641.

Art glassware, made in glassmaking plants
Ash trays, glass
Barware, glass
Battery jars, glass
Blocks, glass
Bowls, glass
Bulbs for electric lights, without filaments or sockets: *mitse*
Candlesticks, glass
Centerpieces, glass
Chimneys, lamp: glass—pressed or blown
Christmas tree ornaments, from glass: *mitse*
Clip cups, glass
Cooking utensils, glass and glass ceramic
Drinking straws, glass
Fibers, glass
Flameware, glass and glass ceramic
Frying pans, glass and glass ceramic
Glass blanks for electric light bulbs
Glass brick
Glassware: art, decorative, and novelty
Glassware, except glass containers for packing, bottling, and home canning
Goblets, glass
Illuminating glass: light shades, reflectors, lamp chimneys, and globes
Industrial glassware and glass products, pressed or blown
Inkwells, glass
Insulators, electrical: glass
Lamp parts, glass
Lamp shades, glass
Lantern globes, glass: pressed or blown
Lens blanks, optical and ophthalmic
Lenses, glass: for lanterns, flashlights, headlights, and searchlights
Level vials for instruments, glass
Light shades, glass: pressed or blown
Lighting glassware, pressed or blown
Novelty glassware
Ophthalmic glass, except flat
Optical glass blanks
Reflectors for lighting equipment, glass: pressed or blown
Refrigerator dishes and jars, glass
Scientific glassware, pressed or blown: made in glassmaking plants
Stemware, glass
Tableware, glass and glass ceramic
Teakettles, glass and glass ceramic
Technical glassware and glass products, pressed or blown
Textile glass fibers
Tobacco jars, glass
Trays, glass
Tubing, glass
Tumblers, glass
TV tube blanks, glass
Vases, glass
Yarn, fiberglass: made in glass plants

323 **GLASS PRODUCTS, MADE OF PURCHASED GLASS**

**3231 Glass Products, Made of Purchased Glass**

Establishments primarily engaged in manufacturing glass products from purchased glass. Establishments primarily engaged in manufacturing optical lenses and ophthalmic lenses are classified in Major Group 38.

Aquariums and reflectors, made from purchased glass
Art glass, made from purchased glass
Artificial flowers, foliage, fruits and vines: glass—*mfpm*
Christmas tree ornaments, made from purchased glass
Cut and engraved glassware, made from purchased glass
Decorated glassware: chipped, engraved, etched, sandblasted, etc.—*mfpm*
Doors, made from purchased glass
Enameled glass, made from purchased glass
Encrusting gold, silver, or other metals on glass products: *mfpm*
Fruit, made from purchased glass
Furniture tops, glass: cut, beveled, and polished
Glass, scientific apparatus: for druggists, hospitals, laboratories—*mfpm*
Glass, sheet: bent—made from purchased glass
Glassware, decorated: chipped, engraved, sandblasted, etc.—*mfpm*
Grasses, artificial: made from purchased glass
Ground glass, made from purchased glass
Industrial glassware, made from purchased glass
Insulating glass, made from purchased glass
Laboratory glassware, made from purchased glass
Laminated glass, made from purchased glass
Leaded glass, made from purchased glass