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RAW MATERIALS USED IN GLASS MAKING

by

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FORWARD

The manuscript for this report was prepared by Mr. Jay Randolph of the Liberty Glass Company, Sapulpa, Oklahoma, and presented at the Mid-Year meeting of the Oklahoma Mineral Industries Conference, held at Tulsa, May 16 and 17, 1941.

In order to make the information compiled by Mr. Randolph available to the public, it was decided to publish the material as a Mineral Report of the Oklahoma Geological Survey.

RAW MATERIALS USED IN GLASS MAKING

The Raw Materials that are required for glass-making embrace quite a number of chemical elements and are either:

1. Minerals prepared by grinding, washing or treating,

   or-

2. Heavy chemicals.

From this combination it may be seen that the raw materials are never perfectly shown by chemical formulas because of the presence of foreign matter or impurities. Compositions calculated on a percentage basis from chemical formulas cannot be strictly accurate but are generally near enough for approximate calculations. This computation of percentages of the different raw materials used in the glass batch is very important and naturally will determine the kind and quality of glass produced.

There are about a dozen varieties of glass being made at this time, as follows:

1. Pyrex glass: A heat resisting type having low expansion and great durability.

2. Thermometer glass: Note: These two types of glass are known as borosilicates as they contain about 10-12 percent boron oxide.

3. Plate glass: This is a soda lime glass with high durability.

4. Window glass: This, also, is a soda lime glass with durability and workability.

5. Bulb glass: This is a soda lime magnesia glass with extreme workability.

6. Glass Tubing: A soda lime magnesia alumina glass with workability and controlled expansion.

7. Tableware: There are two varieties known as (1) Lime Tableware, and (2) Lead Tableware glass. The first is a soda lime magnesia-alumina type, characteristics of durability, workability, and color. The second type of tableware glass is known as potash lead and is characterized by its color, luster, and tone.

8. Optical glass: There are many varieties of optical glass with many different compositions. The three chief types being what is known as:

1. Optical flint glass
2. Optical crown glass
3. Spectacle glass

These optical flint glasses are characterized by fixed optical properties with high homogeneous qualities.

9. Container or Bottle glass: This is a soda lime magnesia alumina type with workability as its chief characteristic.

We have named the different varieties of glass being made, the principal raw materials used in glassmaking, named below, are never all used in any one type of glass. The principal raw materials used in glassmaking together with the trade name of the material, are as follows:

Alumina-	Calcined Alumina
Alumina Hydrate-	Hydrated Alumina
Feldspar-	Microcline (typical commercial spar)
Nepheline Syenite	
Kyanite (90% concen.)	
Kaolin-	China Clay
Cryolite-	Kryolith
Antimony Oxide-	
Arsenious Oxide-	White Arsenic

Barium Carbonate-	
Barium Oxide-	Baryta
Barium Sulfate	Barytes
Boric Acid-	Boracic Acid
Borax-	
Anhydrous Borax	Pyrobar
Burnt Lime-	Quick Lime
Hydrated Lime-	Calcium Hydrate
Limestone-	Calcium Carbonate
Calcium Carbonate-	Whiting
Dolomitic Lime-	Burnt Dolomite
Dolomite-	Dolomitic Raw Limestone
Dolomitic Hydrated Lime	Finishing Lime
Litharge-	Yellow Lead Oxide
Red Lead-	Minium
Bone Ash-	Calcium Phosphate
Iron Oxide-Red-	Rouge
Potassium Hydroxide-	Caustic Potash
Potassium Nitrate-	Saltpeter
Potassium Carbonate-	Calcined Carbomate of Potash
Glassmakers Potash-	Potassium Carbonate Hydroxide
Sand-	Glass Sand-quartz-Silica Sand
Soda Ash-	Commercial Sodium Carbonate
Sodium Nitrate-	Chili Saltpeter
Salt Cake-	Sodium Sulfate
Sodium Silicofluoride	Sodium Fluosilicate
Zinc Oxide-	

The color of certain glasses is of the greatest importance and especial care must be taken in the selection of the raw materials. This is certainly true with regard to the oxides of iron, and minor impurities which tend to discolor the glass. Colorants and decolorizers are used to counteract certain color effects and to furnish the desired color to the finished glass. In the bottle or container glass, it is highly important to obtain a flint glass with correct coloring. An example of this is shown in milk bottles. Here, any blue coloring will immediately cause a rejection of these bottles due to the glass imparting this blue tone to the milk, causing an immediate complaint from the housewife to the dairy. Following is a list of colorants used for glass and the color produced.

Cadmium Sulfide	Yellow
Cobalt Oxide	Blue Violet
Copper	Greenish Blue
Cuprous	Ruby
Cerium	Yellow
Titania	
Chromic Oxide	Emerald Green
Gold	Ruby
Iron Oxide	Bluish Green
Manganese Oxide	Amethyst to purple
Neodymium Oxide	Violet
Nickel Oxide	Violet in potassium glass Brown in sodium glass
Selenium	Pink to ruby on reheating
Sulfur	Yellow to amber
Uranium	Green

The percentage of the batch for colorants is only a small fraction of 1 percent. However, this is a costly item due to the high cost of certain elements, especially selenium and cobalt.

A typical batch for bottle or container glass is as follows:

1,000 pounds	SiO_2	Silica Sand
310 "	Na_2O	Soda Ash
360 "	Al_2O_3	Feldspar
620 "	CaO	Lime (Dol.)
55 "	Na_2SO_4	Salt Cake

In addition, arsenic, selenium, cobalt, and other decolorants and colorants make up a small percentage.

In the selection of any one raw material, it is necessary to carefully consider the percentage of the other elements it contains. As, in the selection of feldspar, the percentage of iron-oxide would be a first consideration, if the color of the glass were vital. The percentage of alumina would have a direct bearing on the melting temperature required. Then the percent of silica must be within certain minimums; for different grades of feldspar, silica sand, and soda ash are the only minerals that are required in every kind of glass, but alumina is used in each type of glass that is herein listed, except optical crown and spectacle. Borax is an important ingredient in pyrex, thermometer, optical crown, and in part of the bottle glass; but the shipping of this mineral to glass plants, I understand, has been stopped by order of the defense board, or at least greatly curtailed.

Generally, silica and boron oxide are the components which lower the coefficient of expansion in glass, the alkalies raise it most, and the other oxides are intermediate.

It is often asked- What is the melting temperature of glass? Glass is never really melted but softened. It has no melting point; but where its viscosity has been so reduced by heating that it reaches a degree of mobility, it is often called melting.

A list of the chemical elements, where they are produced and how they are used in the manufacture of glass, follows. If this paper had covered enamels, pottery, and glazes, the list would probably be doubled. However, practically all the elements here listed are also used in the enamels, pottery, and glazing industries, which industries bear a close relationship to glass.

Alumina: Native alumina is found as the mineral corundum, but the most common occurance is in combining with the silicates, notably the feldspars and clays.

Alumina is also a constituent of bauxite, diaspore, cryolite, sillimanite, andalusite, kyanite, nephelite and many other minerals.

In glass, the most common source of alumina is feldspar, but there is a growing use of the somewhat similar nepheline syenite which has a higher alumina content.

Aluminum oxide, calcined or hydrated, may be used where exceptional freedom from iron is desired, but it is harder to melt. Cryolite is used in the manufacturing of opal glass and kyanite may be used as a means of introducing alumina to the glass batch.

Following is a list of claims for alumina in glass:

1. Lowers coefficient of expansion and hence makes the glass more resistant to thermal shock.
2. Increases crushing and tensile strength making glass more resistant to mechanical shocks.
3. Gives glass more luster and brilliance.
4. Gives longer working range -- suited to machine operations.
5. Increases resistance to weathering and liquids.
6. Increases fusability.
7. Less corrosive to tank blocks.
8. Decreases devitrification which allows faster machine operation.
9. When it replaces silica it makes a more elastic and ductile glass.
10. Lowers annealing temperature.
11. Changes density and thermal conductivity.

Generally speaking, alumina imparts valuable properties to most any type of common glass.

Cost and difficulties of automatic machinery operation limit the amount that can be used advantageously.

Alumina combined with boric acid is important in all types of low expansion glasses such as cook-

Bismuth Subnitrate: Basic bismuth nitrate. Western United States, Peru, and Mexico. It furnishes a pearly luster to glasses.

Borax: Borax added to soda-lime silica glass, improves the durability, lowers the coefficient of expansion, improves resistance to thermal shock and increases the impact and tensile strength. Further, borax in the glass batch facilitates the melting and refining process resulting in valuable production economies. It is produced in California from the minerals kernite (rasorite). They use 50 to 150 pounds of borax per ton of sand in the glass batch. The use of borax narrows the setting range, thus, allowing greater speed on machines.

Cadmium Sulfide: This occurs as the mineral greenockite usually associated with zinc minerals, and is recovered as a by-product in the refining of zinc ores. It is used with selenium in making ruby glass.

Cerium Oxide: Obtained chiefly from monazite, found along the South Atlantic coast of the United States. It is used in the glass industry and is introduced with titanium oxide to produce a very attractive yellow color.

Chromium Oxide: Rhodesia, Russia, Turkey, South Africa, Greece, and Cuba. In glass it is used for green glass.

Cobalt Oxide: Found in Rhodesia, Morocco, Burma, and Canada. It is a coloring medium in glass and a decolorizer. It is the most powerful glass coloring agent known. As little as one part in 500,000 produces a recognizable tint. One part to 5,000 produces a blue sufficient for most ware.

Cobalt is used in combination with either manganese or selenium, usually selenium, for the purpose of masking the yellow. Yellow plus blue equal green which in turn is masked by the complementary pink of selenium.

Copper Oxide: Black copper oxide -- found in Arizona, Montana, Nevada, Africa, Cuba, Canada, Russia and Japan. In glass it is used to make copper ruby colors.

Cryolite: Found in Greenland -- only commercial deposit where it is associated with a pegmatite within an intrusive mass of porphyritic granite. In opal glass, a high percentage is used -- 30 pounds per 100 pounds of batch.

Cullet: Broken or powdered glass. This is a collection of waste glass and broken and imperfect ware and culls. It is crushed and mixed with the raw materials of the new batch. From 1/3 to 3/4 of the total charge for a pot is usually cullet; average 1/5 and rarely exceeds 1/2 total fill for tank of glass. The use of cullet assists in melting and improves the physical properties of the glass. If too much cullet is used there is danger of the glass having a high viscosity.

Decolorizers: A compound in glass batch which tends to counteract the coloring effect of iron or other coloring elements.

Decolorizers may be either physical or chemical and help to produce colorless glass. Only a small part is used in the batch. The following are the chief decolorizers used:

Arsenic Oxide	Neodymium Oxide
Cerium Oxide	Nickel Oxide
Cobalt Oxide	Selenium Oxide
Manganese Oxide	

Iron: High test cast iron is used in the glass industry for molds. Must be close grained for machining and polishing so as to give a high quality surface, hard enough that it will not become scratched easily. Of most importance, it must be able to withstand deteriorating effects caused by contact with hot glass.

Iron in the glass batch may produce in glass any color from yellow through green to bright blue according to the amount of ferric and ferrous iron present. A magnetic pulley in cullet is used to separate any iron found with the glass, as bottle caps, wire, etc.

Kyanite: (Cyanite-Disthene) North Carolina, California, India, Russia. Used as a source of aluminum for glass batches. High aluminum content, ready mixability, low iron content, no appreciable impurities other than silica. It has a low cost. Dissolves readily in glass, if ground to a fineness of 60 mesh.

Lead Chromate: Is used in glass to obtain a deep green color. The chromium imparts color and the lead acts as a flux.

Lead Oxide: Two oxides are used:

1. Litharge or yellow lead oxide.
2. Red lead oxide called minium.

These are used largely in optical glass and tableware. They increase the density and refractive index of glass. Also, the glass can be cut easier than other glasses and has more brilliancy. Lead glasses do not resist the action of acid solutions or weathering conditions as well as the harder glasses.

Lepidolite: (Lithium mica) Found in California, Colorado, South Dakota, and New Mexico. Used in manufacturing opal or flint glass as a convenient source of aluminum. Easily melted due to its lithia and fluorine content. Lowers the coefficient of expansion, thus making for thermal stability and tends to reduce devitrification in the melt. It gives a harder surface and a decrease in brittleness.

Lime: In dolomitic lime, the ratio is some value between magnesium and calcium in certain definite proportions, very close to 56 percent of calcium carbonate to 44 percent of magnesium carbonate.

Lime is one of the most important of the common batch ingredients. Usually, the dolomitic limes or magnesium calcium limes are used not only because of the beneficial effects of the magnesium in the glass batch but also because of the more readily fluxing action imparted to the glass batch by the dolomitic lime.

It is used in the form of crushed stone of various sizes, ground, burnt quicklime, or oxide, and as a lime hydrate.

Lime gives to glass - when added in proper quantities - stability, hardeness, tenacity, and facilitates melting and refining of the metal. It decreases viscosity at high temperatures but increases the rate of "setting" in the working range. It greatly reduces to crushing strength when present in quantities greater than 13 percent.

Burned lime causes too much dust. It saves heat in furnace because carbon dioxide has already been removed. One great disadvantage of burned lime or slacked lime is that burned lime absorbs both CO_2 and H_2O from the atmosphere while slacked lime absorbs CO_2. This causes variation in the composition and introduces errors in calculation of the batch.

Lime is also introduced into the batch in the form of fluorite;a calcium fluoride or as bone ash. Calcium phosphate is used to produce translucent (semi-transparent)opal and opaque (not transparent) white glass such as carrara, alabaster, and moonstone glasses.

Commercial stabilized lime of a fixed composition called Non Feral is used when good color or high light transmission is desired. It is used in optical glass, fine tableware, and certain types of plate glass.

Lithia: Oxide of lithium. In natural ores it occurs as amblygonite, lepidolite, and spodumene. It is a powerful flux, especially when used in conjunction with potash and soda feldspars.

It has low thermal expansion. Also, helps produce a glass having high electrical resistance and desirable working properties. A high content of lithia allows the production of glass that transmits ultra-violet light. Glasses containing lithia are much more fluid in the molten state than the sodium or potassium glass. Lithium is the lightest metal known.

Magnesium Carbonate: Found in Washington and California. It is introduced into various glass batches to allow a lower annealing temperature to increase the melting rate to improve working properties and and to lessen the tendency toward devitrification.

Manganese Oxide: Found in Tennessee, Montana, Virginia. Potassium permanganate is used as a colorant and decolorizer; but for the latter, selenium is now commonly used. In lead potash glasses, this oxide produces an amethyst color; in soda glass, a reddish violet.

Nepheline Syenite: An igneous rock made up of nepheline, potash feldspar, (nucroline) soda feldspar (albite) mica, hornblende, and magnetite. Nepheline is found in Colorado, Arkansas, and Texas. 24 percent alumina content, 60 percent silica, 10 percent soda, and 5 percent potash.

On account high aluminum content, it is a good material for glass batch and melts at a relatively low temperature.

Nickel Oxide: Used for colorants.
1. Green nickel oxide.
2. Black nickel oxide.

Black nickel oxide produces bluish violet in potash glasses and a violet tending toward brown in soda glasses. Nickel is a powerful colorant, one part in 50,000 produces a tint.

Potash: Found in California. The alkali content of glasses runs between 15 and 20 percent. Most of the alkali is soda. The average potash content of flint glass is 7 percent.

Potassium Carbonate: Found in California and New Mexico. It is furnished for glass in both calcined and hydrated form. It is granular and not dusty, entirely suitable for all types of glass production. In the U. S. the cost of potash is several times that of soda. It is only used in high priced ware: optical glass, potash, and lead tableware glass.

Potassium Dichromate: Used in glass for its aventurine effects and is characterized by glittering metallic scales of chromium oxide. It is also used in glass to produce a green color.

Sand: Sand as we speak of it has the formula of silica plus impurities. The iron oxide is the most objectionable impurity. A round and uniform size sand is superior to the angular. Sand will be considered further under the heading of silica.

Selenium: This is a by-product of the copper refining industry. Selenium, together with cobalt oxide, furnishes the best decolorizer for tank glass. One part selenium in 40,000 and 1 part cobalt in 500, 000 are the quantities generally used. Soda lime glasses are successfully decolorized with selenium.

Selenium is also used as a colorant in rose and ruby glass.

Silica: Silica is the most important ingredient in the glass industry. There is no substance used in the glass batch that does not have silica as an important constituent. It occurs as the minerals quartz, tridymite, chert, flint, chalcedony, and opal and in many basic oxide combinations all known as silicates.

There are two forms of silica: crystalline and amorphous, and a third called cryptocrystalline.

The latter type of silica is found in pebbles on the beaches of France. They are calcined and ground to a fine powder and sold as French flint; similar types are found in Denmark and these are used in rotary mills. Quartz is not attacked by acids other than hydrofluoric acid and certain organic acids, and is only slightly attacked by solutions of caustic alkalies.

For the manufacturer of glass, it is necessary that quartz be an essential constituent of the silica rock, but it must be practically the only constituent present.

In the manufacture of glass today, nearly pure quartz sands are used as the source of silica which is the main constituent of all commercial varieties of glass.

Soda lime glass, such as bottle glass, contains from 65 to 75 percent of silica.

The percentage composition of silica sands for different quality glass is as follows:

			Al_2O_3	SiO_2	Fe_2O_3
1st	quality	Optical Glass	0.1	99.8	.015
2nd	"	Flint bottles & tableware	0.5	98.5	.035
3rd	"	Flint	4.0	95.0	.035
4th	"	Sheet Plate & Window	0.5	98.5	.060
5th	"	Rolled Sheet Glass	4.0	95.0	.060
6th	"	Green bottle glass	0.5	98.0	.03
7th	"	Green glass	4.0	95.0	.03
8th	"	Amber bottles	0.5	98.0	1.00
9th	"	Amber glass	4.0	95.0	1.00

A glass sand will be satisfactory and acceptable if all of it will pass a 20 mesh screen and not more than 2-3 percent of it is finer than 80 mesh. Uniformity in composition from different shipments is highly important. Some producers of sand grade their product by the percent of the ferric oxide content.

Sillimanite: (Fibrolite) Same as andalusite and kyanite -- found in South Dakota.

Sodium Carbonate: Soda Ash. It is furnished to the glass industry as 58 percent or 58.5 percent soda ash. It is contained in soda lime glass bottles. Between 14 and 18 percent glass containing soda ash with salt cake produces a harder glass;has a higher softening point; greater strength, and is less viscous.

The price of soda ash and salt cake is now about the same. Salt cake is sodium sulfate.

Sodium Nitrate: Soda Niter. Derived from Chile.

Caliche or atmospheric nitrogen. It is used in glass to oxidize organic matter, help maintain color, and speed up the melt. It has the lowest melting of all glass materials.

Sodium Sulfate: (Salt Cake) Salt Cake is an impure sodium sulfate by-product of the manufacture of hydrochloric acid and sodium sulfate. For use in glass it is free of all iron oxides or sulfates. It prevents the white scum of flakes in a tank of bottle glass and is necessary in certain ratios of soda to lime (less than 2.1)

Spodumene:	SiO_2	63 percent	Lithia	7 percent
	Al_2O_3	28 percent		

Because of high aluminum content, it is harder to melt than feldspar. It is not used even with its high lithia and alumina content because of this high melting.

Sulfur: Sulfur is used in glass as a colorant to produce golden yellow and amber and with cadmium sulfide in selenium ruby glass.

Uranium Oxide: The heaviest known element. The oxides are used as glass colorants. As carnotite, it is found in Colorado, Utah; and as pitchblende in Canada. Rather uncertain as colorants and not much used.

Vanadium Pentoxide: This is a glass colorant producing yellows and greenish yellows.

Zinc Oxide: Most important ores are sphalerite, smthsonite, and calanine.

This is a by-product of Oklahoma zinc mines obtained by reduction of zinc ores. Zinc oxide, distillation of zinc, increases acid resistance of glass and lowers viscosity. It requires a hot furnace. It is better than zinc carbonate.

Zirconium Oxide: Found in Australia, India, and Brazil as the mineral zircon. Function of zircon in glass is about that of aluminum, and in some ways, it is considerably superior. Used in both opaque and transparent glasses.

These are the chemical elements that enter into the production of different varieties of glass. There may be a few more colorants used for black glass, such as metallic sulfides, but in general, the above list embraces the whole field of minerals used in the present day glass.

It might be of interest to note that prices for raw materials and colorants range from $3.00 per ton to over $4,000.00 per ton. The high figure represents colorants only.

As cited in certain instances, before, the selection of raw materials for the glass batch is based primarily upon the percentage of the other elements it contains. In this analysis, the percent of silica is of the first importance, but generally the percent of iron is the next governing factor. Perhaps the next step would be the percent of aluminal with its direct bearing on melting. One feature not mentioned is the percent of raw materials lost from ignition. This is very important and not always given enough consideration. But you may readily see that if you melt 100,000 tons of raw materials per year and you only manufacture 75,000 tons of glassware, the other 25,000 tons have gone out through the stack as gases, dust, or lost in manufacturing. This is why it is very important to study the chemical analyses and carefully note the loss from ignition. This loss varies a great deal in materials with equal chemical analyses. Another factor is the size of the particles and the screen tests should warn you of dust losses.

In reading the different chemical elements herein listed, it seemed that the name of Oklahoma was absent as a state producing any mineral listed with perhaps the single exception of zinc. Of course it is well known that the limestones, salt wells for making soda ash, silica sand, feldspar and many of the chemical oxides used could be, or are produced here in Oklahoma now. But in general, most of the states adjoining Oklahoma, that is, Missouri, Colorado, New Mexico, Texas, and Arkansas are frequently named as producers of minerals that are found within our state.

The writer realizes that Oklahoma has heretofore been about a 100 percent oil state, but it is the aim and purpose of this Oklahoma Mineral Industries group and its affiliated natural resources committees of Tulsa and elsewhere in the state, and in its collaboration with the work of the Oklahoma Geological Survey to expand from this single crop idea of oil and promulgate, not alone a research of Oklahoma minerals, but the actual utilization of all her industrial possibilities.