Science & Glass

For centuries, glassworkers have answered two common questions: **"Where do you get the glass?"** and **"How do you get the colors in the glass?"**

Honestly, you don't have to be a rocket scientist to make glass (although when you get down to the nitty gritty of glass chemistry – it looks a lot like rocket science!). The process of making batch is not much different than whipping up cookies from scratch (not that phony stuff which comes from a plastic tube). Now don't get me wrong, pioneering new colors and reproducing glass melts consistently does take a considerable amount of skill and knowledge in chemistry.

When developing a glass recipe, you have to answer a few questions right from the get-go: How will it be used? Is it going to be blown, cast, pressed, extruded or…what? What type of working characteristics are you looking for: short or long, soft or stiff? How clear does it have to be? Or, if you are you making a color, what type of colorant will you employ? How toxic is it? Will it be compatible with any other glass? How much money do you have to spend? Yes, factors such as price and availability of natural resources come into play. You want to be able to reproduce your recipe consistently (by the ton) if you have to. Simple economics dictate that you do it with the least expensive and most readily available ingredients as possible.

The following information will introduce you to the main ingredients used in making a soda-lime based glass suitable for blowing and casting. It is basic overview of what does what without too much techno-mumbo-jumbo.

You may already be familiar with some glass chemistry, or at least a little bit familiar with making cookies, so let's take a closer look at what's involved.

Soda-lime Glass Recipe	**Chocolate Chip Cookie Recipe**
72.0% Silica sand SiO_2	2 cups flour
14.9% Soda Na_2O	3/4 cup white sugar
7.9% Lime CaO	3/4 cup brown sugar
1.8% Alumina Al_2O_3	2 eggs
1.0% Lithium Li_2O	2 sticks of butter
1.0% Zinc Oxide ZnO	1/2 teaspoon salt
0.5% Barium BaO	3/4 teaspoon baking soda
0.4% Potassia K_2O	2 teaspoon vanilla extract
0.2% Antimony Sb_2O_3	1 bag of chocolate chips

The Sand (or the flour in our cookie recipe)

O.K. we all know that sand (a.k.a. silica, or silicon dioxide) is the main ingredient in glass. (Just like flour is the main ingredient in a cookie mix). It is also called a network former by chemists.

Now we don't melt just any old beach sand to make glass-it has way too many impurities in it. If we melted a batch like that the results wouldn't be crystal clear, rather it would be tinted blue or green. The key to batching good clear glass is selecting the sand with the most desirable characteristics. The sand's chemical composition, its size, shape and method by which it combines with the other ingredients all play important roles in melting glass. In the United States areas in Pennsylvania, West Virginia, and the Mississippi Valley are mined for their quality and purity of glassmaking sand. It is often milled to the coarseness of 100 mesh (roughly the size of sandbox sand) or into flour which helps accelerate the melting process.

For a typical soda-lime glassblowing batch such as melted by the Museum of Glass, the recipe calls for about 72% of silica sand by weight.

Now simply heating sand to 2450°F will not make a suitable glass. (Heating flour up to 350°F does not make a suitable cookie either!) You should add a few select ingredients to give it the characteristics and the tasty intrinsic chemistry, which you very much desire. Sand by itself melts at 3110°F, so it's a good idea to try and lower the sand's melting temperature. You need something to make it flow. You need what's known as a flux.

The Flux-Soda & Lime (like the wet ingredients in our cookie recipe)

Fluxes are present in virtually all glass formulate. To flux the sand, lower it's melting temperature, and make it kinda gooey, we use soda ash (Na_2O) 14.9% soda to be sorta precise.(With cookies you might add 2 sticks of butter). Problem is, if we just used only soda in the glass, the results would be water-soluble. Water, as you know, is an acid and can be quite corrosive or destructive in certain situations.

The other half of our soda-lime equation is the lime. It is also a fluxing agent (or network former) and increases the chemical stability and strength of the glass. In our recipe we call for an addition of 7.9 % calcium oxide, CaO (a.k.a. in their other raw states as: whiting, limestone or dolomite).

The Trace Ingredients

These are the "walk softly, but carry a big stick" constituents. Small additions of other chemicals are included in the batch to sweeten it, balance it and give it some complexity. These "intermediates" are not capable of forming glass alone; rather they assist in strengthening the glass and increasing the working time.

Alumina ($Al_2 O_3$) is added in small amounts (1-3%) to increase the chemical durability of the glass.

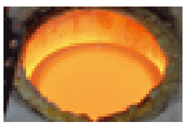
Feldspar ($KNaO\ Al_2O_3\ SiO_2$) is another compound that can impart alumina into the melt, with additional silica and potassium hitching a ride.

Lithium (Li_2O)is also a powerful flux. It is added to soften the glass, decrease its viscosity, and lower its melting temperature.

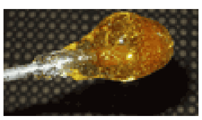
Barium oxide ($BaCO_3$) lowers the melting temperature, decreases the tendency towards devitrification (the formation of crystals within a glass) and offers a higher refractive index. It is also toxic.

Zinc oxide (ZnO) is added to increase the brilliance of the glass. It works well with colors, extends the working time and also reduces devitrification.

Fining Agents



No they are not related to tax collectors; rather fining agents are added to batch to assist in the melting process. When you heat batch to melting temperature of 2450′F there is a great deal of off-gassing by the oxides in the batch. This is a natural and beneficial way the chemicals will combine with each other, insuring a homogeneous mixture. The stuff actually foams up quite a bit! Right after charging the batch looks just like a mélange of marshmallow and cottage cheese. Yum, yum!

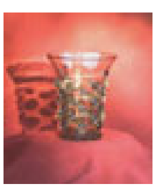


As the batch begins to melt, it creates and traps air bubbles. These air bubbles are not considered desirable by glassblowers. They can be annoying to work with as well as visually distracting to the finished product. A chemical fining agent is added to the mix that will bind with the air /oxygen in the melt and either dissolves it or causes it to rise to the surface and burst.

Arsenic (As_2O_3) and **antimony** (Sb_2O_3) are the two most common fining agents, and both of them are highly toxic. In spite of the tiny amounts used (less than a teaspoon), their inclusion into the batch must be handled with care and only by trained personnel.

Decolorants

Regardless of how pure your source of sand and other chemicals are, you may still end up with a glass that has a subtle tint of color in it. So before I discuss how to get the color in the glass, I must mention something about how to get the color out of the glass.



Some thousand years ago glassmakers in northern Europe lived as close to their natural resources as possible. One such group, in the area that is present-day Germany, were the Waldglas (forest glass) blowers who developed very distinctive styles of drinking and storage vessels, (Not surprisingly considering their affinity for beer!) They fueled their furnaces with wood, and their bellies with bread and ale.

Their sand and other chemicals came from local sources as well, often being less-than-pure by today's standards. So along with the sand and batch mix some trace amounts of **iron** (Fe_2O_3 hitched a ride. The iron imparted a characteristic green tint to the glass and Waldglas products became easy to identify.

Further to the south, and a few centuries later the Venetians discovered a valuable trade secret. If you add a small amount of **manganese** (MnO_2) to the batch, the resulting color it creates will filter

and mask the color generated from the iron and other impurities. This yields a truly colorless glass, which they named "Cristallo" (because it looked as pure as rock crystal). It was the greatest thing since sliced bread (if that was even invented yet).

Demand for this hot new clear glass grew incredibly fast and consequently led to tremendous advances in glassmaking and glassblowing skills. In terms of value glass became as good as gold, or even better. Some works of incredible virtuosity came out of 14th and 15th Century Murano. These pieces have stood the test of time and remain to be some of the greatest works of glassblowing
ever made.

The Venetians made a fortune with their glass. They were to glass back then what Microsoft is to computers today. They created a world-wide market and had a virtual monopoly on their hands, until some young upstarts came along and began offering other products for lower prices and flooding the market with their wares.

What's the big deal with Lead Crystal?

A fellow by the name of Ravenscroft in the late 1600's discovered if you add lead oxide (PbO) to the batch, it acts as a powerful flux (not-too-mention a toxic one at that). The benefit of lead was that it added clarity and brilliance to the finished product. Coldworkers who cut and polished the glass noticed it had great optical clarity with a high refractive index. It became very suitable to make lenses out of this glass.

Other interesting factors that make lead glass so unique: it's much "softer" and has a longer working time, meaning you can blow and manipulate the glass longer with less frequent need to reheat. It also weighs a bit more, so the gathers feel heavier. Oh, by-the-way, lead off-gasses toxic fumes when you melt it, so extra precautions in ventilation must be made so you don't kill whoever gets to charge it.

Colorants (The special ingredients that make it really tasty)

There are several ways to impart color into glass. Most color is created by mixing a specific oxide into the batch and allowing it to react with the other constituents during the melting process. The results depend on a good number of variables, some of which you have control over and some of which you don't. There is still a tremendous amount of trial and error going on in the field of colored glass chemistry as we develop new glasses and try to nail down what does what, and "Can we do that again?" Or, "I hope we never make that mistake again!" It is not surprising that only a small percentage of glassworkers make their own colors. Batching and melting color takes time, money, space, and extensive knowledge of glass chemistry. There are some serious health risks to think about as well.

Most glassblowers today use a pre-manufactured form of concentrated color that is compatible with the clear glass that they are melting in their furnace. These "pigments" are specifically formulated for applications in hot glass. The colors come in every color of the rainbow, either are transparent or opaque. Olympic Color Rods is a glass supply company that carries the Kugler© color line that is used in the Museum of Glass hot shop.

Color is manufactured into rod, frit and powdered forms, and can be applied in a million different ways (or more). That's the fun part. We get color from "Reichenbach", "Kugler" and "Zimmermanni" in Germany, "Gaffer" from New Zealand and "Flying Colors" out of New Mexico just to name few (they are the glassblower's version of "Crayola" crayons). Here's a run-down of the most commonly used colorants. The bulk of them
may be found on the periodic chart #'s 23-29, with #'s 47, 48, 50, 60, 68, 70, and 92 offering additional color possibilities.

Cobalt ($CoCO_3$) – a very small addition of cobalt carbonate will turn your melt a deep dark blue, thus creating the all-time best selling color for glass blowers, cobalt blue. Other blues can be achieved with copper.

Chromium (Cr_2O_3) – adding this to the melt will yield an emerald green color

Copper ($CuCO_3$) – Copper is one of those freaky chemicals that react quite differently with the other constituents of the melt. It is also highly susceptible to the atmospheric conditions of the melting chamber. So, depending on how you melt it, and with what, you can obtain: blues, greens, and even some tasty ruby reds (or if you're off by a fraction, a nauseous liver-brown).

Manganese (MnO_2) – chemists refer to this as a fugitive colorant. It gives rise to: purples, blue/violets, and some browns. Can also be affected by sunlight and U/V.

Silver ($AgNO_3$) – can yield a variety of colors, from yellows to blues, and a wild mix of others depending on how you introduce it to the melt.

Gold ($AuCl_3$) – the most beautiful ruby-red you may ever see. (a.k.a "granny-grabber pink" for its inherent ability to attract a certain member of our society) Gold must be introduced in a chloride form, and it too is very tricky to melt.

Iron (Fe_2O_3) – greens and browns

Cadmium Sulfide (CdS) – oranges, also a challenging color to melt.

Cadmium selenium ($CdSe$) – deep ruby reds. Another tricky color to melt, in that the right temperature and atmosphere must be present in the furnace otherwise it will turn livery/brown.

Opacifiers

You can add **fluorides (CaF_2)** and **phosphates ($Ca_3(PO_4)_2$)** to opacify the melt. Opal glass falls into this category. Fluorine or Fluorspar is used to make white glass. The fumes are toxic, so adequate ventilation must be provided when melting this color.

Specialty glasses

Uranium (UO_3) – can produce yellows, which fluoresce under U/V light. It is no longer produced in the mass quantities of yesteryear for reasons which should seem obvious to you.

Neodymium (Nd2O3) – a dichroic glass made by using this colorant. Some of the sculptures created by the Libenský and Brychtová team incorporate this type of glass with spectacular results.

Dichroic Glass can also be made by a different process where a film of metal is deposited on the surface of the glass by an elaborate and expensive process. (Additional information on Dichroic Glass)

Photosensitive glass – this glass was pioneered over 60 years ago. The Gaffer Glass Company in New Zealand has recently reintroduced it to today's glassworkers. It allows you to create photo-realistic effects within a piece of glass. The artistic potential of this glass is just now being explored, and will undoubtedly yield some extraordinary works n the future.

Coefficient of Expansion

No discussion of glass chemistry would be complete without some mention of this "bad boy." So far the glass chemistry described here seems fairly simple and straightforward. There is one more factor that you must take into account when preparing a batch formula, namely how the resulting glass will heat up and cool down. One can measure how much the material expands (or in this case how much it shrinks upon cooling) over a given period of time. This measurement is what chemists and physicists refer to as the coefficient of expansion. The glass melted by the Museum of Glass has a coefficient of expansion (COE) of 94-96 x 10-7.

The COE is dependent upon the ingredients in the batch. When adding extra oxides into the batch in order to achieve a particular color, you have to realize that those heavy metal additions are somehow gonna tweak the balance a little or a lot. Virtually every gram of every constituent has to be accounted for in any given glass formula. Each and every chemical compound within the batch influences the rate at which the glass heats and cools. This is vitally important when trying to combine two or more colors together. They must have compatible COE's or it will put too much stress or strain in the resulting glass and cause it to crack or (in extreme cases) even explode!

Health and Safety

Why is it that some of the most beautiful glass colors are also some of the most toxic to humans? Perhaps it's Mother Natures way of keeping us in check, or something along the lines of "if you wanna play, you gotta pay" type of equation. Whatever the case may be the fact is there are numerous health risks involved in mixing, storing, and melting glass batch. How you are affected depends upon the nature of the chemical, its route of entry and the length of your exposure to it. There are different methods employed in dealing with the hazards involved, but if proper precautions are taken you can mix and melt batch with little or no exposure to "the elements." Here are a few of the biggies:

Mixing and storing batch

Activities such as mixing and storing of batch should be done in a room dedicated solely for this purpose. The room should be easy to clean, (and kept so), dry, and well ventilated. All chemicals should be stored in airtight bins (water in the form of moisture can reek havoc in batch). They should be clearly labeled and easy to identify. In terms of chemical exposure, the two main routes of entry are through inhalation or ingestion. So don't be snortin' or swallowing this stuff, it'll kill you!

All batchers should wear a respirator when weighing chemicals. They should avoid direct contact with the materials, so using measuring scoops is a good idea. Some chemicals are quick to react with the human body, such as arsenic or antimony which have an acute affect on the internal organs and tissues. In other words, it'll make you sick or kill you in short order.
Other chemicals such as freeborn silica (from that nice clean white sand we're melting) have a more long-term or chronic affect on the human respiratory system. It has a cumulative effect on your lungs. It is called silicosis. Yeah, it can kill ya, but it may take a few years of exposure to do it, (however the effects are particularly painful and not a route you should consider).

Charging and Melting

The charger can protect themselves by wearing a proper respirator for starters. Leather gloves offer usually enough protection for most charging situations, however if encountering extreme heat, some chargers will wear Kevlar gloves-similar to what fire fighters wear. A face shield is usually a good idea to protect against extreme radiation (in the form of blasting heat in excess of 2400′ F.). Adequate ventilation in the furnace area is also a must, especially during charging. You don't want to stir up any more dust than is absolutely necessary. This is why some studios will bag up their batch in 10-50 lbs. sacks. They can then just chuck the whole kit and caboodle into the furnace with no fuss or muss. The bag disintegrates in the high heat and most of the dust stays contained. The other method people use to charge their furnace is to shovel it in, one scoop at a time. It can be quite messy when you spill, and a big chore to clean it all up. Charging duty is usually the entry-level position in any glass shop and relegated to the lowest man on the totem pole. After the first couple of times the novelty wears off and the backbreaking, hot-'n'-sweaty nature of the job hits home. It's grunt work, but if you wanna play, you gotta pay!

Some do's and don'ts of batching

Do:

- Play it safe when mixing batch.
- Get a proper fitting respirator rated for the chemicals you are going to be exposed to.
- Wear clothing appropriate for mixing the batch, and don't take them home with you.
- Keep the ventilation fans running while measuring and mixing batch. Please try and keep the ingredients in the containers and not on the floors and all over the place. Cross contamination of chemicals is not only easy to do, it's a hazard and catastrophe that's easy to avoid.
- Be sure to follow the recipe to the letter when mixing batch. Each and every addition counts. A mistake can be quite costly! I know of one instance where late one night a batcher/charger "forgot" to add the flux to the mixture, and ended up the next morning with a pot full of scummy sand. What a mess and a royal pain to ladle out of the furnace. Needless to say that young man lost his job, and won't ever work there again.

Once again, for the audience at home, Do: Handle batch with care!

Don't:

- You definitely don't want to wear your street clothes when mixing up an ol' ton of batch.
- Don't eat your lunch in the batch room.
- Don't smoke. There are already plenty of reasons not to do that anyway, but it just gets compounded when exposed to the elements of raw glass.

Math at Work

Some useful formulas to know:

p = 3.141592

C = 2pr

Density=mass/volume

Volume cylinder = base x height, or p times the radius squared times the height

V = pr2h

Volume sphere = 4/3pr3

"Do we hafta know this?"

I remember other kids in my 6th grade math class actually asking this brilliant question. Quite often the instructor would roll his eyes and not even dignify the question with a response.

Of course you have to know it! Certain mathematical formulas can and will be very useful to you now or later on in life. If you don't learn and apply it now – (when it's easy) – it'll wind up biting you later down the road, and trust me, it's an awful painful bite when you realize that "Oh Man!, that's something I shoulda learned in the 6th grade!."