<u>Intro to Glaze Technology</u>

What is Glaze?

Glaze is a form of Glass which becomes fused to the ceramic surface during firing. Glaze can be shiny or matt, opaque or transparent, smooth or textured, or stained with a whole range of colours to make earthy, subtle, or vibrant effects.

There are 4 basic constituents to a Glaze.

1. The first is the **glass forming** ingredient to a glaze, eg: **Silica** (or industrial sand). Silica can be obtained naturally from quartz, sandstone, sand, or flint, or it can be manufactured as silica oxide. It has a high melting point.
2. The refractory material **Alumina** (or Aluminium Oxide) acts as a **stiffening agent**. By adding alumina as a clay (kaolin, ball clay, or fireclay) or as alumina hydrate, the glaze can stick to the ceramic surface without coming off. Not only does alumina stiffen a glaze, but it also helps to disperse fine gas bubbles that can form in the firing process.
3. **Fluxes** play the key role in lowering the melting point of Silica, making it usable in ceramic glazes. And like silica, fluxes also promote vitrification (the transformation into glass). The most commonly used fluxes in ceramic glazes are obtained from limestone as **calcium oxides**. Potash feldspar and soda feldspar are also good examples.
4. **Colourants**. Once melted, silica is transparent, making colourants necessary in order to achieve a wide range of hues in glazes. Ceramic colourants are mostly made from **Metallic Oxides** or **Ceramic Stains**.

<u>Glaze Composition</u>

Silica **(Glass Former)** and a source of ***Flux*** **(Melter)** are necessary glaze components. If used alone, however, the result will be a glaze that is too fluid. To increase the viscosity or stiffness of the molten glaze, ***Alumina*** is added to form the **Stabiliser**. The most commonly available sources of alumina for ceramicists are alumina hydrate, ball clays, and kaolins.

Alumina, like Silica, is a refractory material, or a ceramic material with a high melting temperature, so it is used in relatively small percentages.

Besides affecting viscosity, the addition of alumina also increases the opacity and durability of the fired glaze while decreasing its glossiness.

Glass Formers

- Silica (found in nature as quartz, silica is the fundamental oxide that makes up glass and is a primary ingredient in ceramic glazes).
- Talc and Wollastonite are often used as alternative sources for silica.
- Flint (is a finely ground version of silica)

Stabilisers

- Alumina (also adds opacity and a matte surface to the glaze, increasing its hardness, durability, and strength).
- Kaolin (is used mainly as a source of Alumina in a glaze but it also contains small amounts of silica). It comes in the form of China Clay and Eckalite.

Fluxes

Are added to glaze materials to melt glazes at specific temperature. They originate from various sources and can contribute to more than just the melt of a glaze.

Alkaline Fluxes

These contain some form of potassium, sodium, or lithium that causes the glaze to melt. Alkaline glazes tend to be fluid and often have a glossy surface. Intense and brilliant colours may be produced in an alkaline glaze.

- Wood Ash (source of potassium flux)
- Potash Feldspar (contains potassium as the primary flux)

- **Cornish Stone (comprises largely of silica but also contains potassium and sodium)**
- **Soda Feldspar (contains sodium as the primary flux)**
- **Nepheline Syenite (is a potash feldspar that also includes sodium, alumina, and silica)**
- **Borax (composed of sodium and boric oxides, borax is a strong alkaline flux that is used mainly in low fire ceramics)**
- **Soda Ash (is used as a flux in low temperature glazes)**
- **Lithium Carbonate (source of lithium flux, brightens colour of oxides)**
- **Spodumene (is comprised largely of silica, alumina, and lithium, with traces of iron, calcium, and other minerals)**
- **Petalite (a form of feldspar with a high lithium content as well as alumina and silica.**
- **Whiting/Calcium Carbonate (is used as a matting agent and stabiliser in glazes but can also be used as a flux at higher temperatures.**
- **Dolomite (is a natural source of magnesium and calcium oxides. It is used to produce smooth, satin, matte surfaces and promotes crystallization in stoneware glazes)**
- **Bone Ash (is a source of calcium and phosphates that is made from ground animal bones or created synthetically in a lab. It adds opacity and opalescence in high fire glazes)**
- **Wollastonite (contains calcium and silica)**
- **Magnesium Carbonate (magnesium flux used to create satin surfaces. High percentages will produce dry surfaces and crawling)**
- **Talc (used in a glaze as an opacifier, contains magnesium and silica)**
- **Barium Carbonate (contains barium flux that produces matte surfaces and brightens oxides)**
- **Zinc Oxide (zinc flux that has an opacifying effect)**

Frits

The following manufactured frits often contain more than one kind of flux and are stabilised with silica and alumina so that they can be used as a glaze base with other materials.

Frit 3124, 3110, 3134, 3195, 4108

Glaze Colourants

Colouring oxides are naturally occurring chemical compounds that add colour to the glaze base. They may contain other ingredients that also influence the glaze's fluidity and opacity as well as the texture of the surface.

- Chrome Oxide
- Copper Oxide
- Copper Carbonate
- Cobalt Oxide
- Cobalt Carbonate
- Iron Oxide
- Rutile
- Manganese Dioxide
- Yellow Ochre

Stains

Stains are commercially prepared ceramic colourants that are tested for consistency. Like frits, these chemical combinations are fired to stabilize them before being ground into a fine powder that can be used in the place of or in addition to colouring oxides. Stains are usually more expensive than oxides but offer a stable alternative for certain applications.

GLAZE COLOUR

Colour may be achieved on ceramic surfaces by three different methods.

Underglaze

Colourants are applied on top of the raw or bisqued clay surface. A transparent or translucent glaze is then applied, prior to glaze firing.

Glaze

Colourants are added to the glaze batch as part of the recipe. The glaze is then applied to the ceramic piece and fired.

Overglaze

This term is sometimes used to describe two categories.
• Colourants are applied to the glaze surface prior to the glaze being fired.
• Colourants are applied on top of the fired glaze e.g., Enamels and lustres.
These require an additional firing(s) to a lower temperature than the initial glaze firing.

The Formation Of Colour In Glazes

We perceive colour as a wave motion of light.
Longer wave lengths appear red, shorter wavelengths blue.
As it reflects from a material, particular spectral wavelengths of light travels to our eyes, resulting in the sensation of colour. This is reflected colour. Light may also be refracted within a substance before it is reflected, or as it passes through a substance, again altering the wavelength.

Types Of Colour In Glazes

Solution
Colourant particles are dissolved by the glass. e.g., Celadon, turquoise glazes.
Precipitated
Colorant particles are precipitated in the glass liquid, or on the surface of the glaze e.g., Copper red glazes.

Optical (Colloidal)
Particles suspended in liquid glaze which are not coloured themselves but refract and reflect light of certain wavelengths e.g., Chun blue, Boron blue.

Film
Metallic film on top of the glaze surface e.g. overglaze lustre decoration.

Opacity
Opalescent glazes (cloudy - not transmitting light). May be achieved by the addition of an opacifying agent. These materials have a low solubility in glass i.e., they are not easily taken into the melt and remain in the cooled glaze as minute suspended particles, which make the glaze less transparent by refracting and reflecting light.
An opaque glaze totally obscures the original colour of the clay body. A clear or 'base' glaze is rendered opaque by adding an opacifier. These give a cream to white opaque glaze. Opacity can also result from underfiring a glaze.

The opacifiers commonly used are:

Tin Oxide SnO_2. This imparts a creamy white colour to glaze. "Tin glazed" or "majolica" ware has included much of the ware of Persia, Spain, and folk wares of Central Europe. 1-3% gives semi-opaque and cloudy result. Above 6% - 10% gives cream - white.
Zirconium Oxide ZrO_2. A higher percentage of zirconium oxide is needed in glazes to achieve the same degree of opacity. 8% will make most glazes opaque. 12% will produce white. Zirconium is cheaper than tin.
Titanium Oxide TiO_2. Imparts a creamy white opaque colour to glazes when used in amounts of up to 8%. Above this titanium may cause limit pin holing. Alters the shade of colorants and promotes crystal development.

Sources Of Colour In Glazes
Glazes are easily made opaque or coloured by additions of some metallic oxide, either in the form of a refined oxide or a mixture of pre fired oxides known as glaze stains or underglaze colours. The amount of these oxides is generally small and must be weighed accurately.

Glaze Stains or Underglaze Colorants
These commercially prepared colourants and are available in a great variety of colours. They are prepared from metallic oxides but are calcined with other materials to produce colours unobtainable from refined oxides, and to improve colour stability and reliability. For this reason, the colour of stains remain relatively the same before and after firing. Stains are very useful as modifiers of other colours obtained from oxides.

Commercially prepared glazes are sold as a transparent base, to which you may add stains or oxides, or coloured (using glaze stains). Always read the instructions provided with purchased glazes to ensure that your intended application will be safe.

Dependent on the make of stain and glaze composition, 6-8% of stain added to a glaze will produce intense, sometimes opaque colour. Lesser amounts effect a lighter shade.

Oxide Colorants

Colouring oxides are affected by other glaze materials, (especially the fluxes) and the type of firing. The resulting glaze colour effect is dependant on their interaction. Although only a few colouring oxides are used an almost unlimited number of colours can be achieved. The colour of the raw oxide seldom appears the same as the fired glazed colour.

Iron 1/2 - 10%, gives wide range of colour due to its ready solubility in glass, and its sensitivity to changes in the composition of the glaze. Gives tones of yellowish brown to green and dark brown. 1% gives a noticeable tint - over 7% gives dark brown or black. In certain glaze compositions iron can also produce red or blue colours. Iron oxide is an active flux in reduction firing and even small amounts will make a glaze more fluid. Iron is also useful in modifying colours derived from other oxides.
Sources: Usually added in form of:

- Ferric Oxide Fe_2O_3 - red iron oxide.
- Ferrous Oxide Fe_3O_4 - black iron oxide.
- Common red clay contains up to 8% iron.

Copper: 1-5%. In oxidation produces blues and greens, or red in reduction. 1% gives a light tint- 2-3% gives strong colour. More than 5% can result in dark grey or metallic surface. Added to alkaline glazes copper produces turquoise or blue colour and in lead glazes produces various shades of leafy greens. The colour can be modified with other colouring oxides.
Sources:
- Copper Carbonate - light green fine powder
- $CuCO_3$. Black Copper Oxide CuO - coarser in grain size.

Cobalt: 1/8 - 3%. Produces a blue colour which is very intense and gives similar type of blue in almost all types of glazes under various firing conditions. Most powerful oxide in tinting strength - 1/4% is enough for medium blue. Combining cobalt with other oxides will subdue the colour
Sources:
- Black cobalt oxide CoO.
- Cobalt carbonate $CoCO_3$ light purple powder, finer in particle size.

Manganese: 2-9% Combined with iron gives rich shades of cool brown and with cobalt - deep violet or plum colour. In alkaline glazes manganese gives a rich blue-purple or plum colour and in lead glazes gives a softer purple tinged with brown.

Sources:

- Black manganese dioxide $Mn0_2$ - coarse grain size.
- Manganese carbonate $MnCo_3$ - fine pink colour.

Nickel: 1/2 - 8% Can produce a wide variety of colours - most typical brown, mauve, green and grey.

Sources:

- Green nickel oxide $N_1 0$,
- Black nickel oxide $N_2 0_3$.

Chromium Cr_2O_7 1/4-3%. A very strong colorant producing a dense leaf green in most glazes except in the presence of alkaline fluxes, where chrome produces lime greens and yellows, and in the presence of zinc oxide where it may become brown. Chrome may also cause glazes which contain Tin Oxide to become pink.

NB

"The raw colouring oxides such as copper, manganese, iron, chromium and cobalt have been recently shown to affect glaze surface lead release adversely. For this reason, they should not be used in any lead glazes which are applied to surfaces which could come into contact with food and beverages."[1] This also applies to glazes containing Cadmium and Selenium oxides.

Glaze Mixing and Application.

Most glaze materials are supplied already ground to pass through a fine mesh sieve (100 mesh +) and do not require further grinding. The various glaze ingredients are mixed together to disperse all constituent materials evenly.

- Ingredients are first weighed carefully on balance scales, gently mixed in a bucket and then the dry materials added to water. Water to material ratio is usually 3:2 by weight.
- Because inhalation of the fine dusts associated dry glaze materials can lead to respiratory disease, such as silicosis, all powdered ingredients should be handled with care. An approved dust mask should be worn whenever mixing dry powdered materials, and all efforts made to prevent the creation and spread of dust clouds.

[1] Stan Eley, Pottery in Australia". Vol. 10 No.2, page 33.

- After mixing, the mixture is sieved through an 80 or 100 mesh sieve into another bucket. The glaze is then adjusted to achieve correct viscosity. If it is too thick, water is added. If the glaze is too thin, it is left to allow ingredients to settle excess water is then poured off. Sieves and other utensils should be thoroughly cleaned before and after use. The correct viscosity of a glaze varies with the type of glaze and method of application.
- A transparent glaze is nominally the thickness of milk, whilst opaque glazes are usually thicker, like pouring cream. Glazes which are applied by brushing are thicker than those which are sprayed, dipped, or applied by pouring. Many glazes contain heavy ingredients which settle rapidly. To help keep them in solution a suspender such as calcium chloride or Epsom salts is added in small quantities.

Slips and glazes will keep indefinitely, however bacterial action, or the presence of soluble glaze ingredients may alter the viscosity over time. Glazes should be kept in covered containers and may need re-sieving from time to time. If the consistency becomes too hard for use through water evaporation, the glaze should be reconstituted by allowing it to dry out completely, breaking it up, adding water, sieving, and readjusting viscosity.

Glaze Application

Because dust or grease on bisque fired work may cause poor glaze adhesion, the work should be inspected and cleaned if necessary. Glaze may be applied by painting, dipping, pouring, and spraying.

Care must be taken as variations in thickness of glaze application will greatly affect the fired result. This is sometimes used for special effect. When glaze is unwanted on certain areas of an object, water repellent wax is applied to the area and the glaze wiped off once it is dry.

All glaze must be wiped from surfaces which come in contact with kiln furniture or other ceramic work to prevent molten glaze adhesion.

The average glaze thickness should be slightly less that .5mm thick, 1mm is a heavy application. Thickness can be gauged by scratching through the dry glaze with a knife point.

Brushing

Apply glaze in short deft strokes using a loaded soft haired brush. To achieve an even coating, apply 2 or 3 coats of glaze, applying brush strokes perpendicular to the direction of strokes on the previous coat.

Dipping
This method is quick and easily allows an even coating of glaze to be achieved. It is a proven production technique. Work can be completely immersed in the glaze, finger marks touched up later with a brush and smoothed over when dry. Dipping tongs may be used. The dipping requires a large volume of glaze so glaze batches should only be mixed when the quantity of work to be glazed warrants this. Otherwise, valuable resources are wasted.

Pouring
The insides of objects are glazed by filling with glaze then rotating and quickly emptying. The outside of an object can be glazed by supporting upside down over a pan and pouring glaze evenly over its surface. Often used in conjunction with Dipping.

Spraying
Glazes may be sprayed on the work with a spray gun that uses compressed air as a propellant. The technique is a similar technique to spray painting. The object is usually rotated on a banding wheel as glaze is sprayed, enabling an even coating to be achieved. Spray glazing requires very little glaze reserve, so is a suitable technique for glazing individual works or serial production. The equipment requires accurate adjustment, careful handling, and thorough cleaning after use.

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References for Glaze Technology

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DeBoos, Harrison and Smith, Handbook for Australian Ceramics, Sydney, 1984
Hamer, F., The Potter's Dictionary of Materials and Techniques, London, 1992
Hopper, R. The Ceramic Spectrum.

Glaze Resources

Glazy.com - https://help.glazy.org/testing/blending/#line-blends

Ceramic Arts Network - https://ceramicartsnetwork.org/daily/article/Line-Blends-A-Surefire-Way-to-Build-Your-Understanding-of-Ceramic-Glaze-Materials