USE OF DISCARDED BROKEN BOTTLES AS SUBSTITUTE FOR FRIT IN THE MANUFACTURE OF GLAZE

CERAMICS

KOFI BOATENG, B. A. (ART) P G Dip. Art Ed
Technical Managers Dip. In Ceramic Technology

ABSTRACT

Ceramic industries in Ghana depend on fritted materials for the composition of earthenware glazes. These materials which are imported are very costly and not easy to come by.

Glass from broken bottles has been used as a substitute for frit for the composition of earthenware glazes.

Chemical analysis carried out into both the green bottle and the brown bottle indicated that both could be used for the manufacture of ceramic glazes.

Keywords: *Frit, glaze, reduction, oxidation, cullet, crazes.*

INTRODUCTION

Production of ceramic wares demands the use of glazes for the products such as tableware, low tension and high-tension electrical insulators.

Apart from enhancing the aesthetic quality of wares, the strength of glazed pieces is higher and earthenware pieces and sanitary wares are easily washed clean.

Glazes are not manufactured locally, they are imported into the country for use by ceramic industries. The demand for foreign exchange in this direction has brought about scarcity of glazes in the market because of the high cost of glazes and glaze materials.

Earthenware glazes are composed of mainly borax frit and lead bisilicate frit but ceramic industries in Ghana have not developed to the stage where fritting of materials has been undertaken or introduced into pottery production. Studio fritting which involves the heating with oil or gas burner or wood of materials in a crucible to around 1130°C to 1200°C has not started. Both the borax frit and lead bisilicate frit are imported into the country, and 25kg of frit now sells at between £75.38 and £118.95 in the United Kingdom.

Presently in Ghana, many people have set up small scale pottery and ceramic industries for the manufacture of a variety of products ranging from tableware to insulators for low tension wires. And as a result of the Ghana government's drive to promote self-employment among school leavers, there is also a big rush to set up small scale pottery and ceramic industries.

Any local substitute for frit which is easily available and affordable will help sustain the small scale manufacturer and thereby boost production.

The purpose of this study is to find a local substitute for frit which is equally good and can be used safely and cheaply for the composition of earthenware glazes.

Glass has from very early times been used for various kinds of vessels, and in all countries where the industry has been developed there has been produced a great variety of forms and kinds of decoration, much of it of great beauty.

Early Glass

Kofi Boateng

It is not certain in which of the riverine civilisations of the ancient near east glass was first made. The earliest wholly glass objects from Egypt were beads dating from after 2500 BC. Possibly earlier than these was a green glass rod found at Eshnunna in Babylonia that may go back as early as 2600 BC (4).

Some authorities claim that the first glazes date back as early as the 12,000 BC. There were glazed paste beads made in Egypt. The Egyptians discovered glass where sand impregnated with salt; had been fused by a fire. Certainly by 3,000 BC, the Egyptians were using glazes on some of their pottery. These glazes were alkaline copper glazes which were used effectively as decorative coverings. Later in South-West Asia, glazes were used to give extra strength and durability to bricks, wall tiles and pottery.[1]

Glass made from silica, the silicates or analogous glass forming compounds; boric oxide, phosphoric oxide, etc. possesses physical properties in the rigid state which are continuous with those in the fluid state; in other words, glass is a super-cooled or under-cooled melt or solution. Its viscosity which is one of its characteristic and most important properties, varies from that of a thin fluid at a high temperature of 1300°C and above to a rigid condition at room temperature. This property permits the shaping of the mass to form wares and also the removal of stains, which otherwise might be disruptive. [2]

Glazes are super cooled liquids formed by vitreous substances of high viscosity at ordinary temperatures. Silica and boric oxide are the most important glass forming materials.

They produce a covering for ceramic bodies which enhance the beauty of the product. A glaze could be glossy which is highly reflecting or matt which give cool and stable appearance.

The glaze is first attached to the pottery body in the form of a layer of powder. This powder is composed of glass-forming materials, fluxes and stabilisers. During the firing they all fuse together to form a compact layer of molten materials. On cooling, this layer does not separate into former constituents but remain as the new material, glass.

Fritting is the melting of two or more glaze constituents to form a new substance, which is cooled, broken up and ground to a powdered state. Before being fritted, some of these materials are soluble in water and, therefore, unsatisfactory for use in glazes: other materials such as raw lead are poisonous and are made safe for use by fritting. [3]

Table 1 Frit and Glaze Recipes

First Recipe (Frit)	Second Recipe (Glaze)
Litharge 50%	Lead frit 80%
Flint 30%	China clay 20%
China clay 20%	

Earthenware glazes are mainly prepared with frit. In a simple recipe containing litharge, flint and china clay, the litharge and flint could be melted together to form a lead frit and the glaze would chemically remain the same. (Table 1).

The reasons for using the second recipe will be the non-toxicity of the lead glaze, the absence of silica dust (silicosis hazard) and the probable advantage of a glaze that was easier to fire without blistering. [1]

Fritting has advantages of rendering soluble materials insoluble, injurious substances harmless, making some minerals less volatile and giving better glaze fusion. The quality of stiff glazes could be improved by fritting part of glaze materials. Special colour stains can be prepared by heavy reduction. Materials which, by nature' give trouble when incorporated in glaze recipe are fritted.

Borax frit may be prepared with boric oxide which is naturally soluble. Part of the clay is incorporated into the frit batch since excess of raw clay in a glaze causes shrinkage cracks and peeling. Zinc oxide, which make friable, glazes are all fritted together. Glazes are described as under-cooled or super-cooled solutions as the glass. They are glass in their physical and chemical nature, hard, slightly or completely insoluble except in strong acids or bases, impermeable to gases and liquids.[2]

The glaze provides a hygienic covering on pottery because it is smoother than the body it covers and it is non-porous. It is also decorative providing colour, shine and textural contrast with the body; and it increases the strength of the ware by the creation of a body-glaze layer.

Common bottle or window glass which is crushed to suitable finess is known as cullet and has approximate composition 0.5 Na_2O 0.5 $CaO.SiO_2$

It is a raw material which has been found useful as well as cheaper but it is a frit having sufficient water solubility to cause trouble in the mill or storage tank, if left undisturbed for a few hours by settling to form a rather dense cement. This fault may be avoided by the correction of excessive alkalinity through the addition of the necessary amount of acid.[2]

The compositions of the different types of glasses differ importantly according to the product, or, more particularly, the process employed in making the ware. Modern glass batches are subject to very careful chemical control in order to ensure that the physical properties of the molten mass are precisely suitable to the automatic forming process so commonly used.[2]

A coloured soda–lime glass with a clear grey tint and with a shade varying between greenish and bluish contains the elements iron, cobalt and selenium as colouring agents in the weight proportion: Fe_2O_3 (0.25-0.60%) Co (0.0010-0.0040%) and Se (0.0005-0.0030%). The glass is characterised by an excitation purity of less than 6% and a selectivity of more than 1.1. This glass is particularly suitable for automobile wind screen and front side windows.[5]

Mixed alkaline earth boroaluminate glasses comprising BaO combined with at least one of CaO, SO and MgO are useful as frit binders in AlN–Compatible, thick film paste compositions. They are used in the thick – film printing of hybrid microelectronic circuits on AlN substrates.[5]

METHODOLOGY

Raw Materials

These were usually discarded by the breweries. The materials used were glass from broken bottles and Wenchi clay. The brown glass was mainly from Gulder and Guinness while the green bottle was from Star and Club. The Wenchi clay was dug and collected using pick-axes and shovels respectively.

Raw Materials Preparation

The machines and equipment used in the processing of the broken bottles and clay are Jaw Crusher, Disc Grinder, Ball Mill, Sieve, Scales, Storage jars, Blunger, Filter press and dryers.

Processing of Materials

Wenchi Clay

It was crushed when dry, blunged, sieved through 200 mesh, filter pressed, dried, crushed again, and ground and stored.

Broken Bottles

They were crushed ground, ball milled until very fine. The fine powder was sieved through 200 mesh and stored.

Presently bead makers use iron mortars and iron pestles to pound the glass to fine powder. Ceramists can do the same and improve upon such a process since the powdered glass for glaze production should be finer than that for beads.

Care should be taken during processing so that glass dust should not be inhaled since glass contains very high proportion of SiO_2 and silica is the cause of silicosis.

DISCUSSION AND CONCLUSION

The glaze formulated with the brown bottle glass and the clay alone came out beautifully

A glaze with firing temperature of 1150°C was formulated with 20% Wenchi clay and 80% brown bottle glass and oxides introduced in the glaze is as follows:

Table 6: Calculation of Molecular Formula

Mate-rials	Mol. Wt.	Parts by Wt.	Mol. Frac-tion	Yield of oxides in Glaze (Molecular Parts)								
	(A)	(B)	(B/A)	K_2O	Na_2O	MgO	CaO	MnO	Al_2O_3	Fe_2O_3	SiO_2	TiO_2
Wenchi Clay	449.2	20	0.04	0.005	0.000	0.003	0.000	-	0.04	0.002	0.190	0.002
Brown Bottle	265.4	80	0.3	0.003	0.177	0.027	0.090	0.003	0.015	0.018	0..957	-
				0.008	0.177	0.030	0.090	0.003	0.055	0.020	1.147	0.002

Chemical formula for glaze formulated is as follows

0.03 K_2O }			
0.58 Na_2O }	0.19 Al_2O_3 }	3.71	SiO_2
0.10 MgO }	0.06 Fe_2O_3 }		
0.29 CaO			

A second glaze was composed with 10% Wenchi clay and 90% Green Bottle and the oxides introduced into the glaze is as follows:-

Table 7: Calculation of Molecular Formula

Mate-rials	Mol. Wt.	Parts by Wt.	Mol. Fract.	Yield of oxides in Glaze (Molecular Parts)								
	(A)	(B)	(B/A)	K_2O	Na_2O	MgO	CaO	MnO	Al_2O_3	Fe_2O_3	SiO_2	TiO_2
Wenchi Clay	449.2	10	0.02	0.003	0.000	0.002	0.000	-	0.020	0.001	0.095	0.001
Brown Bottle	237.1	90	0.38	0.004	0.213	0.087	0.072	0.004	0.015	0.019	0..072	-
				0.007	0.213	0.089	0.072	0.004	0.035	0.020	1.167	0.001

A glaze with firing temperature of 1150°C was formulated with 20% Wenchi clay and 80% brown bottle glass and oxides introduced in the glaze is as follows:

Table 6: Calculation of Molecular Formula

Mate-rials	Mol. Wt.	Parts by Wt.	Mol. Fraction	Yield of oxides in Glaze (Molecular Parts)								
	(A)	(B)	(B/A)	K_2O	Na_2O	MgO	CaO	MnO	Al_2O_3	Fe_2O_3	SiO_2	TiO_2
Wenchi Clay	449.2	20	0.04	0.005	0.000	0.003	0.000		0.04	0.002	0.190	0.002
Brown Bottle	265.4	80	0.3	0.003	0.177	0.027	0.090	0.003	0.015	0.018	0.957	
				0.008	0.177	0.030	0.090	0.003	0.055	0.020	1.147	0.002

Chemical formula for glaze formulated is as follows

0.03 K_2O }
0.58 Na_2O } 0.19 Al_2O_3 } 3.71 SiO_2
0.10 MgO } 0.06 Fe_2O_3 }
0.29 CaO

A second glaze was composed with 10% Wenchi clay and 90% Green Bottle and the oxides introduced into the glaze is as follows:-

Table 7: Calculation of Molecular Formula

Mate-rials	Mol. Wt.	Parts by Wt.	Mol. Fract.	Yield of oxides in Glaze (Molecular Parts)								
	(A)	(B)	(B/A)	K_2O	Na_2O	MgO	CaO	MnO	Al_2O_3	Fe_2O_3	SiO_2	TiO_2
Wenchi Clay	449.2	10	0.02	0.003	0.000	0.002	0.000		0.020	0.001	0.095	0.001
Brown Bottle	237.1	90	0.38	0.004	0.213	0.087	0.072	0.004	0.015	0.019	0..072	
				0.007	0.213	0.089	0.072	0.004	0.035	0.020	1.167	0.001

Chemical formula for the glaze formulated is as follows:

$0.02\ K_2O$ }		
$0.55\ Na_2O$ }	$0.09\ Al_2O_3$ }	$3.03\ SiO_2$
$0.19\ CaO$ }	$0.05\ Fe_2O_3$ }	
$0.23\ MgO$ }		
$0.01\ MnO$ }		

EXPERIMENTS AND RESULTS

A summary of results is as follows:

Table 8: Glaze Recipe

Glaze BB1 Temperature	1150°C
Wenchi Clay	20
Brown Bottle	80

The above glaze was applied on Fomena clay ware which is brown in colour. It came out smooth, glossy and semi transparent. This beautiful brown glaze is ideal for glazing traditional fufu bowls.

Table 9: Glaze Recipe

Glaze BB2 Temperature	1150°C
Wenchi Clay	20
Brown Bottle	80
Cobalt	3

A colour was introduced into glaze BB1 and the result was smooth, black glossy opaque glaze. This glaze also appears nicely on traditional fufu bowls.

Table 10: Glaze Recipe

Glaze GB1 Temperature	1150°C
Wenchi Clay	10
Green Bottle	90

The glaze matured where it was applied light but bubbled where it was applied thick. The bubbles are easily crushed with finger nails.

Table 11: Glaze Recipe

Glaze GB1 Temperature	1150°C
Wenchi Bottle	10
Green Bottle	90
Copper Carbonate	4

It is a smooth, glossy green glaze

without any problem. When cobalt oxide was introduced into the glaze a very beautiful black glossy glaze was achieved.

The glaze formulated with the green bottle glass and the clay alone did not mature properly at 1150°C, but when copper carbonate was introduced into it, it fluxed beautifully.

The introduction of other oxides such as manganese, titanium, ferric, tin, antimony etc. in both glazes helped in getting a variety of colours such as honey brown, orange, metallic black, yellowish green, ash, and other light colours.

These have self-colour when suspended in a glaze or give colour when in solution in glaze. The solution colour is the colour of the oxide and silica combination and is a dependable result. For example cobalt oxide gives blue and copper oxides gives green. Some colours may be achieved due to the influence of other materials such as lead oxide and zinc oxide which have been introduced into the glaze.

These colouring oxides help bring down maturing temperature of glazes apart from introducing colour. Antimony oxide performs two functions in glazes as an opacifier and as colouring agent. When used on its own, it is not capable of yielding any colour in the melt but it gives yellow in the presence of lead or iron oxide.

Titanium oxide is also used as an opacifier because of its low solubility in a melt. It is added to the glaze to influence its colour by producing opacity to the colour.

Tin oxide in a glaze is an opacifier. It is very important and desirable in colours for underglaze and overglaze decoration.

The results obtained so far indicate that only few materials are needed for the formulation of very good glazes, namely glass, clay and colouring oxides and opacifier.

Ceramists will be able to manufacture their own glazes with between 90 and 100 percent materials from local sources.

Broken bottles are abundant locally. Entrepreneurs need crushers, grinding machines and ball mills to process these broken bottles.

Fritting demands the use of foreign materials such as B_2O_3, Pb_3O_4 and other machines and equipment, and expertise which can be avoided altogether when glass is processed for use.

Although the glass itself is a glaze it has to be adjusted to suit the body on which it is applied, as glaze-body-fit is very important.

Addition of flint is necessary where crazes are observed. Clay helps to suspend glaze particles and keep them from settling. It also increases the alumina content in the glaze, which prevents the glaze from running.

Manufactures should try to process the glass to a very fine particle size of about 200 mesh sieve in order to expose the particles to a large surface area to help quick solid solution.

With the introduction of glazes made from bottle glass, ceramists should be able to produce their wares at cheaper cost in order to compete with foreign goods which have flooded the market.

REFERENCE

1. Hamer, F. The Potter's Dictionary of Materials and Techniques, First Published in Great Britain by Pitman Publishing, 39 Parker Street, Kingsway, London WC 2B 5pB page 144-5, 139
2. Parmelee, W.C. Ceramic Glazes, Published by Industrial Publications, Inc., 1951 Page 94-5, 13.
3. Clark, K, Pratical Pottery and Ceramics, Published in Great Britain by Studio Vista Publishers, Blue Star house, Highgate Hill, London N19, 1972 page 63.
4. Encyclopaedia Britannica Vol. 10 page 456, 466.
5. Mattox D.M., Aluminium nitride-compatible thick-film binder glass and thick-film paste composition Published Ceramic Abstract in association with CERAM Research (UK) and The American Ceramic Society, Vol. 76 No 3 October 1997 Cambridge scientific Abstracts page 14 and 17.