DEVELOPMENT OF SHEET STEEL GROUNDCOAT ENAMEL FROM LOCAL RAW MATERIALS

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DECLARATION

I, Peter Nnaji Okolie, declare that this thesis is solely the result of my work and has never been submitted anywhere for any degree. All literature cited have been duly acknowledged in the bibliography.

P.N. Okolie

CERTIFICATION

This Project thesis entitled DEVELOPMENT OF SHEET STEEL GROUNDCOAT ENAMEL FROM LOCAL RAW MATERIALS by PETER NNAJI OKOLIE meets the regulations governing the award of the degree of Master of Science (Chemical Engineering) of Ahmadu Bello University and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

To the memory of my late brother in-law Godwin Ngwu and sister Francisca Ginika Okolie who both passed away during the tenure of this work. May their souls rest in perfect peace, Amen.

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There could be no greater service to any individual than the opportunity to widen his horizon and find fulfilment through educatiion. For making this knowledge possible and available to me, its my sincere wish to acknowledge the effort of many people.

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ABSTRACT

An investigation into the development of sheet steel groundcoat enamel from local raw materials was carried out. These local raw materials included: feldspar, quartz, magnesite, whiting, baryte and manganese dioxide.

Several formulations were made. Of the five formulations that yielded best performance properties, enamel B had the highest local input of raw materials of 84 percent, followed closely by D with 78 percent, then A with 71.5 percent, C with 68 percent and finally E with 64 percent. Borax or boric acid constituted about 95 percent of the foreign input.

The raw materials were smelted and fritted using the quenching method of fritting. Complete fusion of batch raw materials was attained after 1.5 - 3 hours. Enamel E had the lowest maturing temperature of 1080°C, followed by A with maturing temperature of 1115°C, C and D had 1150°C maturing temperature while B matured at 1200°C.

The enamels were applied on low carbon sheet steel test pieces. Firing was carried out at 840°C - 880°C for 4 -12 minutes. Firing at the higher temperature range for shorter-time yielded better performance properties than at lower-temperature range for longer time. The enameled samples were tested for fundamental performance properties. The coating thickness varied from 0.40mm - 0.48mm.

When heated and quenched for eight successive temperatures of 170, 175, I8O, 185, 190, 195, 200 and 205°C, the enameled samples showed no signs of crazing, flaking off or cracking. When exposed to a 10 percent solution of citric acid for 15 minutes, enamels B, D and E showed no damage in appearance and relative cleanabi1ity while A and C failed this acid resistance test. There were no resultant damage to the enamel coating when subjected to impact test. The order of gloss and desired colour is:

E > A > D > C > B

When compared with industrial standands 1_1 and $I_{2,}$ all the formulations A, B, C, D, and E yielded successful performance properties but enamel E proved most successful.

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LIST OF ABBREVIATIONS

ASTM	:	American Society for Testing and Materials
BS	:	British Standards
BSI	:	British Standards Institution
FOS	:	Federal Office of Statistics
GSN	:	Geological Survey of Nigeria
LOI	:	Loss on Ignition
NIS	:	Nigerian Industrial Standard
NSO	:	Nigeria Standard Organisation
RMRDC	:	Raw Material Research and Development Council

LIST OF NOTATIONS

$A, A_1, A_2, A_3, A_4, A_5$ = Formula A, Slip formulations for Formula A.

$A', B', C',$ = Property factors for ingrients A,B,C

a,b,c,d,e = Points on an enameled test piece

$B, B_1, B_2, B_3, B_4, B_5$ = Formula B, Slip formulations for formula B

$C, C_1, C_2, C_3, C_4, C_5$ = Formula C, Slip formulations for formula C

$D, D_1, D_2, D_3, D_4, D_5$ = Formula D, Slip formulations for formula D

$E, E_1, E_2, E_3, E_4, E_5$ = Formula E, Slip formulations for formula E

Ec = Modulus of elasticity of composite

Ee = Modulus of elasticity of enamel

Em = Modulus of elasticity of metal

I_1, I_2 = Industrial standard enamels

K = Thermal conductivity W/m^oC

K_1, K_2 = Constants

P	=	Enamel property being calculated
Q	=	Thickness of metal/Total thickness of composite
Ro, R_2o	=	Basic oxides
Ro_2	=	Acidic Oxides
R_2O_3	=	Neutral (Amphoteric) oxides
T, DT	=	Temperature, Temperature diifference ^oC
X_A, X_B, X_C	=	Weight percentages of each ingredient
α	=	Alfa
ρ	=	Rho, density kg/m^3
η	=	Eta, integer
μ	=	Mu, mesh opening, micrometer

CHAPTER ONE

1.0 INTRODUCTION

Enamel is defined as a vitreous or glassy inorganic coating bonded to metal by fusion at a temperature above 430oC (Lee(1961)). A coat applied directly to the base metal is called the groundcoat which functions as the intermediate layer between the metal and the cover coat which provides the final surface. Into the making of enamel goes such materials as feldspar, borax, quartz, flourspar, kaolin, magnesite etc. These materials are usually fritted to render soluble materials insoluble, reduce the toxicity of toxic materials, reduce excessive shrinkage during firing of enamelware and to attain better and more uniform colours.

Enamel frits used in enamelware industries in Nigeria are mainly import. The problem imposed by inadequate foreign exchange in recent years has affected the enamelware industry very adversely with a consequent increase in the prices of the enamelwares. The demand for enamelwares both for domestic and industrial purposes has been on the increase annually. The availability of steel resources (iron ore) and the presence of steel plants as the Delta Steel and the Ajaokuta steel plants and numerous steel rolling plants favoured the choice of steel as a base metal for both domestic and industrial applications in Nigeria.

The demand for enamel coating because of its higher protective and decorative qualities over ordinary organic coatings for steel and the high foreign exchange spending on enamel frits - combined to stimulate the search for local sourcing of the enamel. The object being to replace most of the ingridients in the enamel frits with locally available substitutes.

This investigation is aimed at determining these local raw materials suitability for groundcoat enamel frit production and determining their performance properties. In this report, literature on groundcoat enamels and the local raw materials are reviewed. The general groundcoat application techniques and metal preparations are also presented.

CHAPTER TWO

2.0 SURVEY OF LITERATURE

This survey of literature contains an up-to date documentations of the origin and past works on enamels and especially sheet steel groundcoat enamels. This includes historical background, economics and uses, classifications, composition and raw materials, milling, metal preparation, enamel properties, defects and controls.

2.1 Historical Background

Enamelling is an old art which dates back to the 4th century B.C. It was perhaps first practised by metal workers in Asia and Europe for the purpose of covering silver or copper jewelry with colonred enamels. The first commercial enameling of sheet steel and cast iron was accomplished in 1850 in Germany and Austria (Lee(1961)).

Porcilain - enameled metal art objects have been identified with early civilizations in the middle East, specifically in the Mediteranean area and the Orient. It is believed that the knowledge of techniques for creating decorative porcelain enameled objects was passed from one Mediteranean group to another. The Egyptians, Greeks, Romans, Spaniards and Arabs practised this art.

2.2 Uses and Economics

Porcelain enamel as a coating on metal performs many important functions. It protects the metal against corrosion, decorates the metal and resists the attack of alkalies, acids and other chemicals. It is a sanitary coating importing no odour or taste. Porcelain enamels are used to provide readily cleanable surfaces and to provide special effects like electrical, optical and chemical effects.

Because of its sanitory aspects, its protective and strengthening function to the metal, and its decorative character, porcelain enamel has been genersally adeopted as the most suitable material for bathtubs, laundry appliances, ranges, sinks and refrigerator liners. The decorative and corrosion-resistant aspects of this coating have led to its many uses in architectural applications. Because of extremely low porosity and resistance to chemical attack, the enamel has found widespread use in the dairy, pharmaceutical, brewing and chemical industries. Porcelain enameled tanks and vessels made of heavy - gauge sheet steel or cast iron are commonly used in these industrial applications.

2.3 Classification for Enamels

Enamels can be classified in a number of ways Common classifications (Othmer (1965)) are as follows:

1. According to Function:
   - Groundcoats;
   - Cover coats;

2. According to Service:
   - Acid resistant;
   - Alkali resistant;
   - Hot water resistant;
   - Chemical resistant;
   - Abrasion resistant;
   - Electrically resistant;
   - Thermal shock resistant;

3. According to Composition:
   - Alkali borosilicate;
   - Titannia;
   - Lead-bearing;
   - Leadless enamels;
   - Phosphate;

4. According to Metal Types:

- Sheet steel (low carbon, enameling iron, enameling steel);
- Cast iron;
- Aluminium;
- Copper, gold, silver;
- Stainless steel;

5. According to Decorative Character:

- Clear;
- Colored;
- White;
- Stippled;
- Matte;
- Glossy;
- Semi-Matte;
- Beading;

6. According to Opacifying Material:

- Titania;
- Zirconia;
- Antimony Oxide;
- Molybdenum

7. According to Method of Application:

- Wet process;
- Dry process;

8. According to Type of Product:

- Appliances;
- Cooking utensils;
- Sanitary ware;
- Chemical equipment;
- Jewelry;
- Architectural panels;
- Signs;
- Hot - water tanks;

9. According to Firing Temperature:

- Hard/high fire (845-880^{o}C);
- Medium temperature (800-845^{o}C);
- Low temperature (730-800^{o}C);

2.3.1 Classification of groundcoat enamels

According to Martin (1973), porcelain enamel groundcoats are primarily of three types:

1. Sheet steel groundcoats which are smelted borosilicate glasses with cobalt, nickel and manganese oxides present for adherence.
2. The cast iron wet process groundcoats which are usually semi-vitreous in nature.
3. The dry process cast slush groundcoats which are smelted borosilicate glasses without or with a minimum of cobalt, nickel or manganese as adherence promoting oxides in the smelt.

2.3.2 Classification of sheet steel groundcoat enamels

The various types of sheet steel groundcoats fall into several categories based upon maturing temperature and method of use (Martin (1973)). That is whether the groundcoat is fired at a higher temperature and or longer time than the covercoat or whether it is used as a 'high speed' groundcoat in which the groundcoat land covercoat are fired in the samee time-temperature cycle.

Many of the current production steel groundcoats are fired either at a higher temperature or a longer time than the covercoat. In a large number of plants however andd particularly those which have only one continuous furnace, the groundcoat is fired in the same time-temperature cycle as the covercoats. This type of operation requires the so-called high speed groundcoats which must fire out at a relatively low temperature in a short time cycle. Groundcoats of this type in addition to being fast firing, must not sag, boil or blister when refimed at their median burning temperature when the cover coat or covercoats are applied.

2.4 Enamel Composition and Raw Materials

Enamels can be formulated with a wide range of physical and mechanical properties including a good degree of hardness and excellent chemical resistance. The basic ingredient of all enamels is a glass or frit made up primarily of inorganic compounds or minerals.

The compositions of the ground and cover coats differ. The combinations used depend on the specific application. When the ware is to be subjected to temperature variations, the metal will expand or contract. In such applications, both the ground and covercoats must have coefficients of thermal expansion or contraction similar to that of the base metal.

The basic materials used in enamels may be classified into six major groups:

1. Refractory materials eg. silica or Kaolin;
2. Fluxing materials eg. lead oxide, zinc oxide, borax, soda ash, cryolite, fluorspar etc;
3. Opacifiers eg. tin oxide, antimony oxide, sodium antimonate, zirconia, titania etc;
4. Colouring oxides eg. oxides of cobalt, copper, iron, nickel, manganese etc;
5. Floating agents eg. clay, bentonite, gums, ammonium alginate etc;
6. Electrolyters eg. magnessium carbonate, borax, sodium nitrite, potash alum, soda ash, ammonium carbonate, sodium aluminate, calcium chloride, magnesium chloride, epsom salts etc.

Since porcelain enamels are substantially glassy coatings, the composition is based on glass-forming ingredients. The principal glass formers are B_2O_3, SiO_2, and P_2O_5. Other glass formers such as GeO_2, As_2O_3 are

impart unusual properties for enamel glasses. Phosphate glasses although low melting and commercially economical are generally not sufficiently resistant to alkali attack.

While it is difficult to describe the specific action of each ingridient in the porcelain enamel composition, some generalities csan be expressed as follows:

1. An increase in SiO_2 content increases firing temperature and acid resistance and lowers the expansion coefficient.
2. An increase in alkali content decreases firing temperature and acid resistance and raises the expansion coefficient.
3. An increase in the Al_2O_3 and ZrO_2 content increases alkali resistance.

Most sheet steel groundcoat enamels are cobalt bearing. Table 1 shows typical compositions of cobalt blue groundcoat enamel for sheet iron and steel (Lee(1961)).

Table 1: Compositions of Cobalt Blue Groundcoat Enamel for Sheet Iron and Steel

Ingridients	Batch Weight Percent						
	1	2	3	4	5	6	7
Feldspar	36.3	30.9	27.0	22.0	20.5	28.0	33.5
Borax	35.6	25.2	30.0	30.0	39.5	32.0	37.0
Quartz	14.6	19.6	20.5	29.0	22.5	20.0	19.2
Soda ash	7.4	6.4	9.8	5.0	5.0	6.0	5.6
Soda niter	-	5.0	5.0	4.6	4.7	2.3	-
Fluorspar	5.3	7.5	6.0	5.0	6.0	3.0	3.9
Red lead	-	-	-	-	-	8.3	-
Cobalt oxide	0.2	0.4	0.5	0.4	0.4	0.2	0.3
Manganese oxide	0.6	0.5	1.2	2.0	1.0	0.5	0.5
Nickel oxide	-	-	-	1.0	0.4	-	-

2.4.1 Nigerian enamel raw materials

The Nigerian enamel industry development depends on an abundant supply of raw materials. Nigeria is blessed with a large number of mineral resources for the enamel industry as presented in Table 2. Figure A2 of Appendix F is the mineral resources development map of Nigeria as reproduced

from GSN (1987). Some of the raw materials are in mere existence as they are not capable of being worked economically at least for now. The profitability of the mineral deposits depend upon the cost of winning, treating, transporting and marketing the products upon the price they command in the market and upon the degree of support or protection afforded by Government through trade and taxation policies.

Distances in Nigeria are great, railways are few and road transport is expensive. This has a serious effect on the development here of low priced minerals which cannot sustain large charges for handling and transport.

The chemical minerals which are important in enameling industry include salt and brines, borax, nitrate, sodium carbonate, potash, sulphur, calcium and magnesium oxides. Sulphur is perhaps the most important chemical mineral but unforttunately, occurence of native sulphur has not been reported in Nigeria GSN (1987). Salt is used in the manufacture of industrial chemicals like soda, sodium bicarbonate, caustic soda etc. However, the few indigenous sources of salt are by no means sufficient for the country's needs most of which have to be met by imports.

Much of the country has already been examined by geologists but is would be premature to say that there are no further deposits of useful minerals awaiting discovery.

Table 2: Nigerian Enamel Raw Materials

Raw Material	Function	Location
Baryte	Flux	(Cross River),(Benue),(Gongola),(Plateau),(Anambra)
Beryl	Flux	(Plateau), (Kwara)
Bismuth	Flux	(Plateau), (Benue)
Clay	Refractory	Jos(Plateau), Kankara (Katsina),(Sokoto),(Gongola), (Anambra), (Imo), (Ogun), (Ondo), (Bendel).
Feldspar	Refractory	Egbe-Okene (Kwara), Oshogbo, Ijere (Ondo) Gwoza (Borno), Abeokuta, (Gongola)
Fluorite	Flux	Afu hill (Plateau), Akwana-Arufu (Benue)
Glass Sand	Refractory/ Glass former	Enugu, Port Harcourt, Ughelli, lLagos, (Imo), (Ondo).
Iron Stone	Colourant	Mt. Patti (Kwara), Agbaja, Birnin Kebbi, Igala area, Udi hills (Anambra).
Kyanite	Refractory	Sabon Birnin Gwari (Kaduna)
Lead	Flux	Zurak, AbaKaliki, (Plateau), (Benue), (Gongola), Izon (Niger).
Limestone	Flux	NKalagu, Calabar, Ukpila, Ewekoro, Yandev, Sokoto, Ashaka, Jakura.
Manganese	Flux	Itobe (Benue), Elebu (Kwara), Burum (FCT), Igbetti (Oyo), Tsa-Kasinta (Gongola).
Manganese	Colourant	Calabar, Bamenda, Zaria-Funtua.
Mica	Refratory	Kabba-Egbe (Kwara), Calabar.
Molybdienite	Opacifier/ Adherence	(Kwara), (Benue), Bendel), (Niger).
Phosphate	Glass former	Abeokuta, (Ogun), (Imo), (Sokoto), (Bendel)
Quartz	Refractory	Okene, Oshogbo, Ijero, Gwoza
Salt	Discoloriser	(Benue), (Anambra), (Imo), (Cross River), (Plateau), (Sokoto), (Gongola), (Bauchi).
Sillimanite	Refractory	Ibadan (Oyo)
Soda Ash	Flux	Tula, Geidam, Yusufari, Manga (Borno).
Tatania, Thorium Zircon	Opacifierr	Jos and other Nigerian alluzal concentrates

Table 3: Summary of Chemical Composition of Major Local Raw Materials

S/No.	Material	Oxide Composition (%)						
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	LOI
1	Feldspar (Okene)	65.5	18.9	0.20	0.1	15.3		0.1
2	Quartz (Okene)	99.9		0.2	0.1			0.1
2	Clay (Kankara)	44.5	38.64	Nil	1.30			16.7
4	Magnesite (Tsa Kasimta)	4.7	1.0	0.5	3.5	42.1		48.4
5	Whiting (Jakura)	1.17	0.42	0.14	94.79	0.84		2.69

2.5 Smelting and Fritting Operation

Soluble materials are not suitable for direct addition in the enamel mixture but must be rendered insoluble by incorporating them in an insoluble glass refered to as frit. Fritting also renders toxic materials less toxic, reduces excessive shrinkage during firing of the enamel-ware and helps to attain better and more uniform colours.

2.5.1 Fritting rules

As an aid in the proper compounding of frits, certain empirical rules have been derived which are helped in the proportioning of the enamel ingredients. The rules only serve as a guide as it is possible to prepare satisfactory frits which violate one or more of the empirically derived fritting rules. The necessary fritting rules as summarised by Permelle (1973) is as follows:

1. The ratio of the RO group to the RO_2 should be between 1:1 and 1:3. This is to assure the ready fusion of the frit.

2. The ratio of the alkalies in the RO group to the rest of the members in the RO group should not be more than 1:1. This is to make certain that the frit is insoluble. The alkali content makes the frit soluble.

3. The ratio of the B_2O_3 to the SiO_2 should bo no greater than 1:2. This is to assure that the frit is insoluble.

4. The alumina content of the frit should not exceed 0.2 equivalents. This is to aid in ready fusion of the frit.

In most frits, it is desirable to have at least 0.05 equlvalents of alumina as it usually brings about a better balanced frit.

2.5.2 Fritting process

In fritting, the raw materials are weighed out and mixed thoroughly in a ball mill or mixing mill. There are different techniques used in fritting a mixture. Two methods suggested by Lee (1961) are:

1. Drip frit furnace
2. Quenching;

When small batches or experimental batches of less than 45 Kilograms are to be prepared, they can be melted in a crucible type furnace. This is known as the drip frit furnace procedure. The crucible is generally made of fireclay with a small hole in the centre of the bottom. The crucible is set in a small pot furnace. When heat is appiled to the outside of the crucible, the material inside gradually melts and runs out through the bottom hole. As

the mixture melts, additional raw stock is fed into the crucible. The melted material is collected in a water - *filled container placed underneath the crucible.* An alternative method is to use the same type of furnace, melt the whole batch in a solid crucible, remove the crucible and pour the molten frit into water. This is called quenching. The principal purpose of quenching is to make the frit more friable.

In commercial fritting of large quantities, pot furnances or rotary smelters are used. This can be periodic but in most cases it is a continuous operation. The frit batch is fed in at one end and the melten frit flows out and into water. It is then dried after which it is ball milled to the desired particle size distribution. Decomposition of materials, gas evolution and solution of decomposed materials occur during fritting, (Othmer(1965). Figure 1 shows operational sequence for fritting operation.

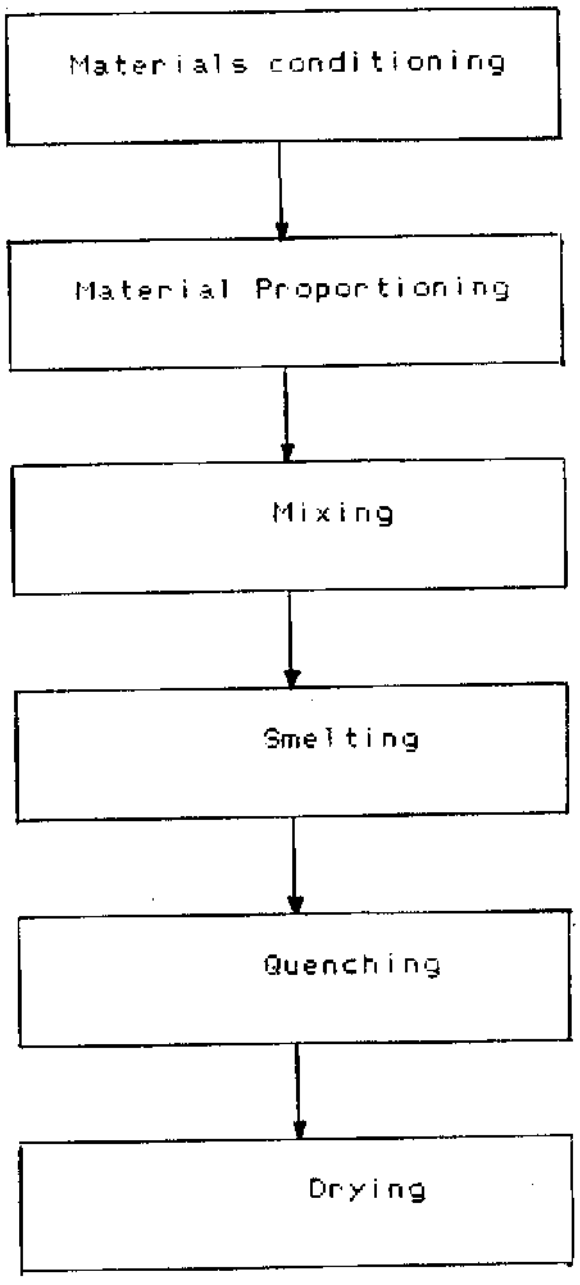


Figure 1: Fritting Operation Flow Scheme

2.6 Milling Operation

The frit is a friable material easily reduced to small particles by a ball-milling operation. The breaking up of the glass frit into small-sized particles is carred out either wet or dry (Othmer(1965)). Dry powders are used for the dry process cast iron enameling. Dry powders are also prepared and marketed for the subsequent preparation of slurries and slips used in the wet process application techniques.

For sheet-steel enamelling, the porcelain enamel frit is ball-milled with clay, certain electrolytes and other mill additions and water to form a stable suspension. This clay- spported slurry of small frit parctiles is called slip and has a consistency similar to that of a thick coffee cream (Othmer (1965). The ingredients comprising the mill batch are carefully controlled. The amount and purity of all materials in the mill including the clay and water affect the rheological character of the slips as well as a number of properties of the fired enamel such as acid resistance, reflectance and gloss.

Ball mill grinding is accomplished with porcelain or high-alumina balls 1.27 - 5.08cm in diameter. Ball size, mill speed, mill charge and ball charge are important parameters in determining the optimum milling time required for optimum size distribution in prepared slip. Groundcoat

enamels are ball-milled to a fineness of 95 percent of solids smaller than 0.0074cm (200 mesh). Covercoats are ground finer to 98 percent of solids finer than 0.0044cm (325 mesh) (Othmer(1965)).

2.6.1 Mill room practice equipment

The following pieces of equipments are used to accomplished milling (pemco(1961)):

1. Ball mill with dense, non-porous spherical porecelain balls.
2. Pestle and mortar for experimental batches
3. Scales - it is advisable to have an accurate grain and or gram scale for measuring very small or experimental quantities.
4. Screens are provided for screening enamels before use. Mechanical secreening devices are far uperior to stationary screens.
5. Magnetic seperators - permanent magnet or electric magnets.

2.6.2 Milling criteria

Pemco (1961) recommended that the ball charge should always be kept at 50-55 percent volume of the mill for the most efficient milling. One-half of the balls should be 5.08cm in diameter and the balance of the balls should be

2.54 - 1.27cm in diameter. Worn down balls should be replaced. The water content of the mill should be carefully controlled as excess or insufficient water increases milling time. The mill should be charged to the rated capacity as increasing the frit charge increases grinding time while decreasing frit charge causes excessive wear on linning and balls.

Table 4 shows the mill speeds for given diameters of mills as recommended by Pemco (1961). Reduced speed decreases efficiency of milling while excessive speed is disadvantageous.

Table 4: Mill Speed for Given Diameters of Mills

Inside Diameter of Mill(cm)	R.p.m. of Mill
228.60	17
182.88	20
152.40	23
122.00	25
91.44	30
76.20	35
61.00	35
45.72	40
30.50	40
Laboratory Jar Mill	50-60

Mill should be charged up to three-quarter mark with frit and other mill additions. Materials are weighed with an accuracy consistent with the volume of material being added. Materials are generally added to the mill in the following order: oxides and or opacifiers first: electrolytes; clay; frit; and finally water.

Fineness of the milled enamel is controlled by the grinding time while specific gravity is controlled generally by water content of the slip. After the mill has run the proper number of revolutions or for the proper length of time, a sample of enamel is removed and tested for fineness. If this test shows that the enamel is still too coarse, the mill should be run until it tests to the required fineness. Table 5 shows the characteristic of fineness of grinding of several commercial enamels as recommended by Pemco (1961). Mill may be drained with gravity flow to discharge it or if large quantities are to handled, it may be emptied by air pressure. Screening can take place as mill is emptied. For initial screening, a coarse sieve of either 20 or 30 mesh (0.083 or 0.054cm) is satisfactory. This is followed by 40 or 50 mesh sieve for sheet iron groundcoat and 50 or 60 or even possibly 80 - mesh sieve for sheet iron covercoat enamels. After screening enamel should pass through a magnetic seperator. Some iron contamination will probably occur from door frames but magnetic seperation will remove most of it.

Table 5: Characteristic of Fineness of Grinding Enamels

Enamel	Specific Gravity	Gram Residure on 200 Mesh from K100g sample
Sheet iron ground coat	1.60 - 1.65	4 - 8
Sheet iron white covercoat (antimony bearing)	1.80 - 1.90	2 - 6
Sheet iron while covercoat (antimony free)	1.80 - 1.90	1 - 3
Sheet iron coloured covercoat	1.80 - 1.90	1 - 3
Sheet iron black edge	1.80 - 1.85	1 - 4

2.6.3 Mill Additions

The quantity of each material to be used as a mill addition is generally given by the frit manufacturers. Minor deviation from these recommendations may however be necessary. Once the proper mill additions have been determined, they should be adhered to rigidly. The following go into the making of balanced enamel slip (Pemco(1961)):

1. Clay - clay in enamel acts in the following ways:
   - Acts as a floating agent,
   - Acts as a binder for the dry or bisque enamel
   - Has an opacifying action;
   - Acts as a refractory to increase the firing temperature or extend the firing range;
   - Affects the structure of the fired enamel.

2. Bentonite - Bentonite is a highly colloidal type of clay having about five times the suspending power of ordinary clay.

3. Feldspar, Nepheline Syenite and Quartz. These materials are added in small amounts to the mill batch to increase firing temperature or firing range of some enamels.

4. Opacifiers - Opacifiers are added to increase the covering power or reflectance of white enamels. They are not generally used in excess of 4 percent. Opacification is due either to fine subdivision of opaque particles of opacifying agent or to creation of extremely fine bubble structure in enamel gloss which acts to distract light striking the surface.

5. Colouring oxides - Colouring oxides are added as mill additions to white enamel to produce pastel colours. They are used generally with clear frit to produce strong or brilliant colours. Colourants are composed of metallic oxides. Stability of colours varies from

one colour to another and also with type of enamel. Colourants are seldom added in amounts in excess of 4-5 percent. Oxides generally increase refractoriness of enamel glass. Table 6 is the guide to the use of colourants as reported by Nelson (1966).

6. Electrolytes - Electrolytes act to flocculate the clay and promote suspension of the enamel frit particles in the slip. Electrolytes most commonly used with various enamels as reported by Pemco (1961) is shown in Table 7. Care must be taken not to use excessive amounts of electrolytes as excessive amount destroys gloss of enamel.

7. Water - Minerals carried in solution in water may act as electrolytes and this mineral content may vary from place to place with variations in water hardness: Therefore deionised water is preferable and it may be necessary to install water softening plant.

Table 8 lists typical maxima and minima for the most common mill additions and slip characteristics of sheet steel groundcoat as recommended by Pemco (1961).

Table 6: Guide to use of Colourants

Colour	Oxide	Percentage	Temperature	Atmosphere
Black	Cobalt	1 - 2	Any	Either
	Manganese	2 - 4	Any	Either
	Cobalt	1	Any	Either
	Iron	8	Any	Either
	Manganese	3	Any	Either
Blue	Cobalt Turquoise	0.5-1	Any	Either
	Copper Slate blue	3 - 5	Low	Oxidizing
	nickel	1 - 3	Low	Oxidizing
Brown	Rutile	5	Any	Reducing
	Chromim (with MgO, ZnO)	2 - 5	Low	Either
	Iron	3 - 7	Any	Oxidizing
	Magnanese	5	Any	Either
	nickel (with Zinc)	2 - 4	Any	Either

Green	Copper	1 - 5	Any	Oxidizing
	Gray-green hon	1 - 4	Any	Reducing
	Nickel-Magnesia	3 - 5	Low	Oxidizing
Red	Pink Chrome and Tin	5	Any	Oxidizing
	Coral-Chromiem	5	Low	Oxidizing
	Purple-Manganese	4 - 6	Any	Oxidizing
	Copper	1	Any	Reducing
	Iron	2 - 5	Low	Oxidizing
Tan	Iron	2	Any	Either
	Manganese	2	Any	Either
	Rutile	2	Any	Either

Yellow	Antimony yellow stain	3 - 5	Low	Either
	Uranium yellow	5 - 8	Low	Oxidizing
	Zirconium Vanodium stain	5 - 10	Any	Either
Pure white	Tin	5	Any	Either
Weak blue white	Titanium	8 - 12	Any	Either
White	Zirconium	8 - 12	Any	Either
Weak yellow white	Atimony	10 - 12	Any	Oxidizing
White	Ziropax (frit)	10	Any	Either

Table 7: Electrolytes Most Commonly Used with Various Enamels

Enamel	Electrolytes	Normal Formula limit per 100kg
Sheet iron groundcoat	Borax	500-750g
	Magnesuim Carbonate	0-255g
	Sodium nitrite	0-255g
Sheet iron covercoat	Magnesuim Carbonate	127.5-255g
	Sodium nitrite	0-255g
Sheet iron acid	Potasium carbonate	0-255g
Resisting covercoat	Ammonium carbonate	0-625g
	Sodium aluminate +	
	Sodium nitrite	0-255g
	Sodium aluminate +	
	Aluminate calcium chlride	0-255g
Cast iron enamels	Magnesium carbonate	172.5-255g
	Sodium nitrite	0-127.5g

Table 8: Typical Optimum for Common Mill Additions and Ship Characteristics of Sheet Steel Groundcoat Enamels

Mill addition/Characteristic	Optimum Value
Frit	100kg
Clay	11-22kg
Refractory	0-44kg
Borax	0-1kg
Magnesium Carbonate	0-375g
Bentonite	0-375g
Odium nitrite	0-375g
Milling fineness	4-12g/200 mesh
Specific gravity	1.58-1.64 dip
	1.62-1.68 spray
Pickup	250-40g/m^2 cylender
Application weight	90-250g/m^2
Fired thickness	0.005-0.015cm
Water content	37-42 percent

2.6.4 Milled enamel storage

In addition to providing a bank of milled enamel, storage allows aging of enamel. Enamel should be allowed to age for 8-24 hours before being used. Aging permits the enamel to cool and allows entrapped air to escape. Excessive aging is deleterious to working properties however particularly for the acid-resiting enamels. Storage tank should be metal lined with porcelain enamel. Tanks should be equiped with blunger or paddle which should be run periodically to prevent enamel from settling in the tank. Blunger should be run one minute in every five (Pemco(1961)).

2.7 Metal Preparation

Sheet-metal parts are formed by the well-known processes of stamping, bending and shearing. Welding if needed is carried out in such a way that the welded joints can be enameled without defects. Enamelling cannot be successful unless the metal is thoroughly cleaned and kept clean until the enamel coat is fired. The cleaning and pickling process is a preparation of the metal base (Othmer(11965)). Figure 2. is the operational sequence of the metal preparation process.

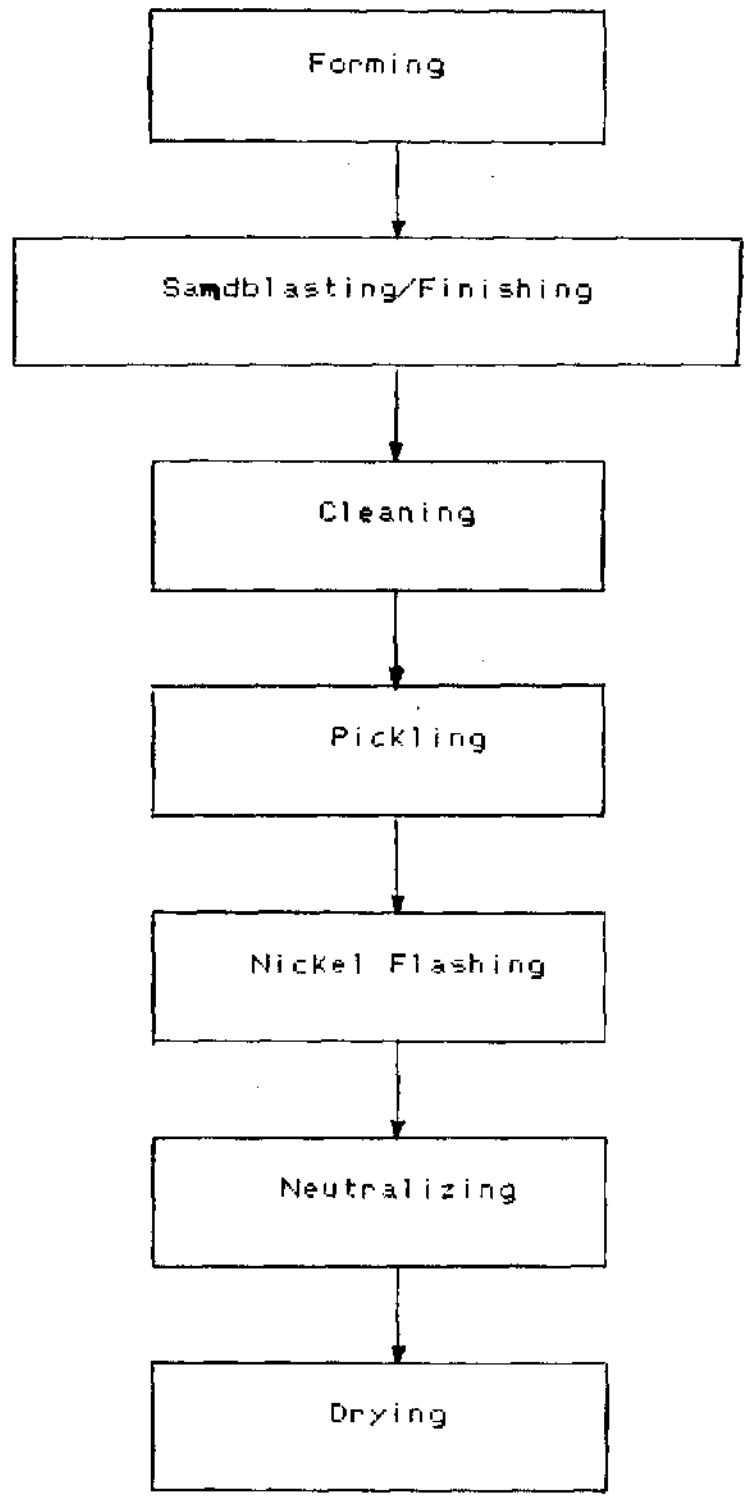


Figure 2: Metal Preparation Sequence

2.7.1 Metal cleaning and pickling process

Metal cleaning and pickling process generally requires sandblasting, washing in a boiling solution of a cleaner, rinsing in water, immersing in hot/cold chemical solutions and finally rinsing in water. The last rinsing operation is critical and important because it has to remove all traces of acid.

The pickling solution generally contains 6 percent sulphuric acid by weight and is heated to a temperature of 65-70^{o}C. If hydrochloric acid is used, the concentration is 11 percent and the solution is kept at room temperature. In some operations, an additional pickling operation is required in order to eliminate fish-scaling. This is a nickel dip process which gives a better bond with the groundcoat. The solution contains nickel sulfate and ammonium sulfate with sufficient acid or base to give the desired hydrogen ion concentration. It is used at a temperature of 70-80^{o}C. The metal is immersed in the solution for a period of 5-10 minutes (Lee(1961)).

Nickel dip solutions can be made by adding 110g of double nickel salt, 7g of boric acid and 7g of ammonium carbonate to 4 litres of water. The neutralizing solution is made of 3-4 percent of alkali (sodium oxide) made up of soda ash, borax or trisodium phosphate and water. This bath is heated to a temperature of 65-70^{o}C for maximum

efficiency. After the metal products are removed from the neutralizing solution, they are immediately dried.

The composition of the cleaning solution depends upon the type of the oilm grease and solid material to be removed, including the amount and type of drawing compounds used in the metal forming operations.

Where oil or greases are present which cannot be removed by ordinary cleaning methods or when strain has been created in the forming process which must be relieved before the enamelling operation is begun, anealing or burning off is necessary. Here the ware is placed in a muffle furnace at 660-720^{o}C and heated until all the oil or grease is burned off. Operation may require from one to three minutes or longer depending upon the amount of oil covering the ware and upon the weight of the load entering the furnace (Lee(1961)).

2.8 Sheet Steel Groundcoat Enamelling

Sheet steel groundcoat enamelling operation consists of metal preparation, enamel application drying and firing of the enameled ware. Figure 3 is the flow scheme for sheet steel groundcoat enamelling process.

Sheet steel denotes steel cold-rolled and supplied in the shape of flat sheet. The chemical composition of the steel sheet used in enamelling shall be as stated in Table 9 (NIS(1974)).

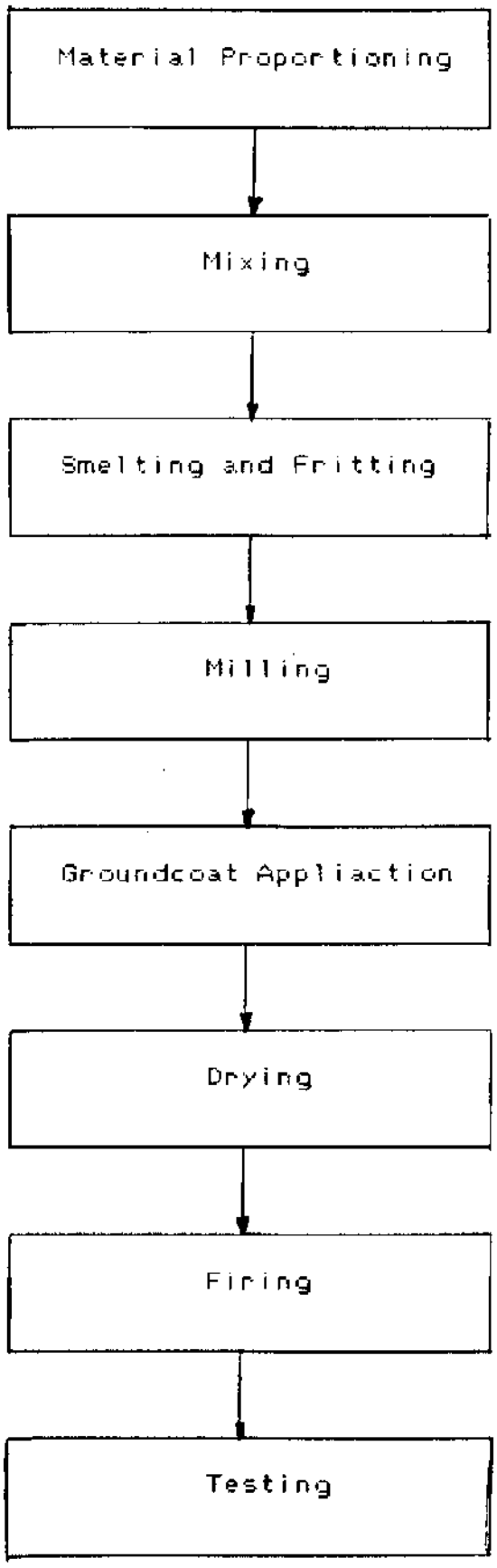


Figure 3: Flow Digram of Sheet Steel Groundcoat Enamelling

Table 9: Chemical Composition of Enamelling Sheet Steel

Type	Carbon Max.%	Manganese Max.%	Phosphorue Max.%	Sulphur Max.%
Ordinary	0.15	-	0.060	0.060
Drawing	0.12	0.50	0.050	0.050
Deep Drawing	0.10	0.50	0.040	0.040
Extra Deep Drawing	0.10	0.50	0.035	0.035

2.8.1 Application methods

Application of sheet steel groundcoat enamels generally occurs immediately after the metal ware is prepared. Enamels can be applied by dipping, spraying and or slushing.

Dipping is usually prepered whenever possible since it is a more economical process. Labour costs are lower and frits usage is reduced since a thinner weight can be applied more evenly and handling or processing losses of the materials are minimized. In selecting a piece of ware to be dipped, it is necessary to ensure that the shape is regular enough that the enamel will cover all faces, will drain uniformly over the area and will not hang-up on brackets or reverse flanges. In dipping operation, the ware is immersed in a dip tank and shaken with a pair of tongs to throw off any excess enamel.

Where dipping is not desirable or feasible, the groundcoat is usually sprayed either by automatic spray or individual hand spray guns. The automatic spray machines are the more economical and deposit a more uniform coating of enamel on the metal surface. Many parts are so designed that they do not lend themselves to automatic spraying and must of necessity be entirely hand sprayed.

Some parts which either because of design or weight of the part are impossible to dip or spray are slush dipped. In slushing, the enamel may be applied to the ware by bucket or hose and allowed to drain into a sump. In many cases, it is desirable to 'cup' or slush the wet groundcoated piece in the area of drain streak with additional enamel in order to eliminate or minimize the drain streak (Martin(1973)).

2.8.2 Enamelling furnace

The furnace is the heart of every enamelling installation since other pieces of equipment depend upon the size and design of the furnace. Enamelling furnaces may be divided into two principal types (Smith(1978)).

1. Box-type furnace - Here a single load of ware is fired at a time.
2. Continuous furnace - Here the ware is loaded at one point and discharged at another point.

Furnaces may be muffle type, fired with oil or gas. Electricity is sometimes used as a direct source of heat without muffle. Gas may be used as radiant tube furnace without muffle. Firing may be intermittent or continuous. The furnace should be designed to heat the ware from room temperature to firing temperature in minimum time. Prolonged drying or slow heat will induce tearing on the enamel surface. With a box type or intermittent furnace, time must be allowed for the furnace to recover firing temperature after the cold ware is placed in the firing zone. Intermittent furnaces usually require 5-15 minutes for recovery. In continuous furnaces, the enamels can be fired from room temperature to maturity in 8-12 minutes depending only upon the weight of the charge and the time required for the mass to reach top temperature. The speed of the continuous furnace can be adjusted to compensate for the varying masses being fired. Condition of operating parts of furnace should be checked at regular intervals. Cleanliness of all operating parts is the rule.

2.8.3 Drying and firing

Enamels should be dried as rapidly as possible after the application. If allowed to stand around, especially in groundcoat application, rusting may take place. Drying is accomplished by application of heat and circulation of air around the parts to be dried. Theoretically, the most satisfactory drying conditions are those in which drying

takes place from the metal out, the outside being the last to dry. Too repid drying may cause tearing or curling or similar defects. Rate of drying should be as uniform as possible over entire surface. Operating temperature of dryer need not be above 150°C. Air circulated through dryer for drying purposes should be clean. Here again, cleanliness of all operating parts is the rule.

The operation of fushing an enamel on metal is known as firing or burning. It is during this process that the groundcoat enamel developes a bond between glass and metal. The enamel, applied to the surface of metal in finely ground particles of glass, fuses together to form a dense, homogeneous mass of the desired physical properties such as resistance to acid, abrasion, and dirt or discoloration. In a continuous tunnel-type furnace, each coated item progresses through the furnace supported on firing racks especially designed to withstand long service at the repeated cycles of heating and cooling. Gradual heating and cooling of the ware occur more with continuous firing than with intermittent methods. Furnace temperature in the hot zone of continuous furnaces and box furnaces is established to mature the coating in a matter of minutes. Groundcoasts firing in a box furnace would be on the order of 3-6 minutes at 850-880°C. Covercoat firing is generally carried out at shorter times and slightly lower temperatures. Enamel firing temperature is of course relatted to the coating

composition, the metal thickness and the type of metal (Othmer(1961)).

The various stages through which the enamel composition passes on its way to the finished glassy coat may be briefly enumerated as: dissociation of the original component, chemical combinations, sintering, fusion and crystallization. These operations are well defined but frequently overlap and may be repeated in some degree as the temperature rises and new compounds appear and disappear. When enamel begins to fire, first it turns black, then it starts to melt and draws up into pockmarked little balls. At this point, some banemental is exposed between the tiny enamel nodules before the melting enamel softens and spreads over it again. If a blast of cool air from the open furnace door should strike the exposed metal at this time, firescale will form quickly and will likely interrupt the normal fusing process. All sorts of aggravations can result. The enamel may leave most of these scaly spots completely bare, pits can form, discolorations may occur in the enamel or partly fired lumps may congeal and stubbornly resist later firing (Nelson(1966)).

2.9 Properties of Enamel

Each pocelain enamel composition is dessigned so that certain fundamental performances of the enamel are realised such as;

- Good adherence to substrate
- Thermal expansion fit to the metal and residual stressess.
- Desired chemical properties such as acid resistance, hot water resistance or alkali resistance
- Desired physical properties such as abrasion resistance, thermal shock resistance, high gloss, high reflectance and desirable colour.

2.9.1 Good adherence to substrate

It has been known that cobalt bearing materials incorporated in the frit composition would enhance the adherence of the enamel to sheet steel and that adherence and wetting are associatted. Under oxidizing conditions, the enamel glass wets the metal and the oxide on the metal surface tends to dissolve into the enamel layer. Under reducing or neutral conditions for enamel firing, the oxide originally on the metal surface becomes completely dissolved and the glass then fails to wet the metal surface.

Othmer (1965) stated that the mlechanism of adherence can be considered to fall into two main types. One is physical adherence involving the physical gripping of the

glass by a rough metal surface roughened mechanically prior to enamelling or roughened during enamelling by the corrossive attack of glass on the metal and by dendritic attachments to metal forming during the enamel - firing treatment. The other adherence mechanism involves the chemical bond of the metal, metal oxide and enamel glass. Adherence in porcelain enamel terminology generally refers to the amount of glass remaining in an impacted fractured area of the porcelain enamel system.

2.9.2 Thermal fit and residual stresses

During firing, porcelain enamel glass becomes less viscous as temperature is increased. At the elevated temperatures, the enamel is relatively fluid and it conforms to the configuration of the metal surface. As the coating is cooled from the high temperature of firing (850-880^{o}C) the fluid glass does not maintain a stress for any measurable length of time. As cooling proceeds, the coefficient of expansion (or contraction) of the coating exceeds that of the steel and tensile stresses begin to develope in the coating. The tensile stress continues to increase on cooling until the expansion coefficient of the glass equals that of the metal. As cooling continues further and the coefficient of the glass becomes less than that of the metal, the tensile stress in the coating decreases and compressive stress developes (Othmer (1961)).

Thermal expansion comparisons of coatings and metals have often been used in the determination of residual

stresses in the coatings. Residual stress analysis must take into account the cooling rates, the viscosity characteristics of the glass, the relative thickness of the metal and coating and the modulus of elasticity of coating and metal throughout the temperature range in which stress is developed. At high temperatures, the glass behaves essentially as a viscous material, changing to viscous elastic to principally elastic as the temperature decreases. Thermal expansion values can be calculated from measurements of thermal deflection of enamel - metal composites. Thermal expansion coefficients in the temperature range of 0-300°C can be calculated using additive formula by Othmer (1961):

$$P = A'X_A + B'X_B + C'X_C + \text{---------- (1)}$$

Othmer (1961) listed factors for calculating thermal expansion for various oxides and further gave the linear expansion coefficients for common materials in the porcelain enamel system as shown in Table 10.

Table 10: Linear Expansion Coefficient for Common Enamel Materials

Material	Linear Expansion Coefficient
Steel	11.7×10^{-6}
Groundcoat	$10-11\times10^{-6}$
Covercoat	$8-10\times10^{-6}$
Aluminium	23.5×10^{-6}
Cast iron	10.5×10^{-6}

The modulus of elasticity of the composite system of enamel glass and steel has been shown to lie between the modulus of the glass and that of the metal. Othmer (1961) reported that the composite modulus can be calculated by the expression:

$$E_c = Q^3 (E_m - E_e) + E_e \quad \text{----------} \quad (2)$$

Othmer (1961) also reported some physical properties of enamel glass as shown in Table 11.

Table 11: Physical Properties of Enamel Glass

Property	Value
Density	2.5 - 3.5 (g/ml)
Hardness	5-6 (moh's scale)
Tensile strength	$3.45\text{-}10.34 \times 10^7$ (N/m^2)
Compressive strength	$1.38\text{-}2.75 \times 10^9$ (N/m^2)
Modulus of elasticity	$5.5\text{ -}8.27 \times 10^{10}$ (N/m^2)
Dielectric constant	5 - 10

2.9.3 Desired chemical properties

The resistance to alkali and acid attack is evaluated on the basis of loss in weight, loss in gloss or cleanability of the surface. A citric acid spot test (10%) is used as a room temperature test for acid resistance of glossy light-coloured enamels. In the spot test, loss of gloss and cleanability are determined in a qualitative manner.

2.9.4 Desired physical properties

Porcelain enamel is considered the most scratch resistant and hardest of coatings. In surface abrasion, the rate of abrasive wear increases with time and in subsurface abrasion which follows, the constant higher rate of wear continues. Abrasion resistance can be evaluated by the loss of gloss or loss of weight.

Resistance of porcelain enamels to failure by thermal shock was developed for enamels for cooking utensils and other items subjected to high temperatures in service. Thermal shock tests involve repeated cycles of heating and quenching with water. Heating for each successive cycle is carried out at progressively higher temperatures. A vissible fracturing as evidenced by spalling constitutes a failure. Water is an especially severe quenchant. Thermal shock failures with water result from the water vapour entering the enamel layer at the instant of shock. This water vapour condenses in the crack and in the bubbles of the enamel near the cracks. On subsequent heating, the entrapped water expands to cause spalling to the enamel layer. Thermal shock resistance is a direct function of enamel thickness. Thin coatings provide excellent thermal shock resistance (Othmer (1961)).

Other physical properties as impact resistance, good appearance etc. are also desirable in the enamel composition.

2.10 Property Defects

Deviations from perfect continuity in porcelain enamel coating and unusual departures from smoothness are given in certain descriptive terms that developed with the porcelain enamel technology. Groundcoat defects and groundcoat - covercoat defects may be caused by faulty base metal, improper fabrication; improper cleaning procedures, general plant operational procedures including drying and firing as well as groundcoat - covercoat formulations. Martin (1973) listed some of the more prevalent defects especially in groundcoat enamels as:

- Fishscale
- Hairlines
- Sagging
- Blistering
- Copperheads
- Tearing
- Pitting
- Pinholes
- Bisque damage
- Orange peel
- Water streaking
- Reboil

2.10.1 Fishscale

Fishscaling appears as a semi-circular fracture in the enamel surface from which the chip has usually been removed and are similar in contour to the scale of a fish. There are three types of fishscales, two of which namely process fishscale and delayed fishscale usually make their appearance in the covercoat while the third so called shinnerscale is purely a groundcoat defet. In all cases, the actual defect is caused by gas pressure at the groundcoat-metal interface due to the pressure of hydrogen gas comming from the metal at the point of poor adherence. Shinnerscales appear as very small chips on the groundcoat surface and are due to an over firing of the groundcoat.

2.10.2 Hairlines

Hairlines are defects which make their appearance in covercoats either as dark or light coloured usually present in a stress pattern. This defect is caused by stresses in the metal which cause a break in the enamel surface during the early stages of firing operation. These stresses may be due to improper design, improper fabrication or to non-uniform heating of large parts in the enamelling furnace.

2.10.3 Sagging

This is a sheet steel groundcoat defect which makes its appearance after covercoat firings giving the covercoats the appearance of having run or rippled. The defect occurs only

on ware which has been fired in a vertical plane. The basic cause of groundcoat sagging is the inability of a given groundcoat to retain sufficient viscosity at covercoat maturing temperatures. During firing of the groundcoat and subsequently as the covercoats are fired, the groundcoat absorbs iron oxide from the base metal. Since iron oxide is a flux in groundcoats, it makes the groundcoat adjacent to the base metal more fluid so that the groundcoat flows under the covercoat during covercoat firing.

The best remedy but one which is not always feasible is the use of a harder or higher firing groundcoat and or a lower firing covercoat therby producing a groundcoat-covercoat combination in which the groundcoat is more viscous at covercoat firing temperatures. A nickel dip in the metal preparation cycle is very beneficial in slowing down the oxidation rate of the base metal and in reducing the amount of iron oxide that the groundcoat must absorb. Increasing the refractory mill addition is also of assistance but is limited by the groundcoat maturing temperature.

2.10.4 Blistering

Blisters can usually be traced to the presence of some contaminants foreign to good enamilling practice. Since blisters denote the presence of some agents foreign to good enamelling operations, they can to a large extent be controlled by rigid inspection and adherence to the commonly accepted practices of good enamelling and good house-

keeping. Blisters are often times caused by an excessive amount of water vapour or sulphur gases in the furnace. Excessive groundcoat application thickness will cause blisters or boiling due to underfiring of the groundcoat in the first fire and in the subsequent complete burning of the groundcoat in the covercoat fires.

2.10.5 Copperheads

Copperheads are sheet steel groundcoat defects which have the appearance of darkened copper coloured depressions in the enamel. The consensus is that these reddish - brown spots are concentrations of the oxides of iron in a silicate matrix resulting from saturation of the groundcoat with iron oxide at that point. Since a copperhead is the result of excessive localized oxidation, any step in enamelling which will minimize such localized oxidation during firing or the rusting of the base metal before firing will reduce copperheads. The presence of excess chlorine in water, mill additions or the furnace atmosphere will cause copperheads.

2.10.6 Tearing

Tearing or crawling is a seperation type defect which is more common to covercoats but is occassionally found in groundcoats. In groundcoats, the defect is almost always caused by a dirty metal surface. It may also be caused by excessively fine grinding, high application weight or flexing of groundcoated parts in the bisque stage. Where tearing is present and it is impossible to apply a thin coat

and to grind at a normal fineness, sodium nitrite additions are very effective.

2.10.7 Pitting

Several incidences of groundcoat pits have recently been traced to poorly functioning magnetic seperators which were not removing all the magnetic iron in the groundcoat slip. Excessive electrolytes in the groundcoat mill formular or excessive aging of the milled enamel will also pit most groundcoats.

2.10.8 Pinholes

Pinholes are a function of the groundcoat and the cleanness of the metal surface. Close examination of pinhole defects will usually show that the defect goes down in the metal and that a depressed copperhead is present in the bottom of the pinhole. A more fluid groundcoat with a higher borax addition may be of assistance in minimizing some of the defects.

2.10.9 Bisque damage

Spray or dip groundcoat is usually handled in the bisque in transfering the ware from the dryer to the furnace. Damage resulting from handling can best be controlled by excise of care in handling but failing this, additional bisque strength in the groundcoat is required. Increased clay or bentonite and decreased borax or sodium nitrite will usually strenghten the bisque. Harder drying may be of some assistance.

2.10.10 Orange peel

Orange peel of sprayed groundcoats is undesirable and adversely affects the quality and appearance of the ware. The advent of low pressure spraying equipment has helped considerably in reducing the amount of orange peel with spray groundcoats or covercoats. In general, spraying at the proper set, minimum air pressure and optimum angle of incidence and distance from the ware will minimize spray orange peel.

2.10.11 Water streaking

Water-streaking or 'rat tail' is chiefly a hollow ware defect, although it occasionally appears on flatware. It is caused primarily by an excessive relative humidity in the dryer which will supress surface evaporation of water long enough to permit the water in groundcoat slip to run and erode the surface of the coating. Maintenance of low dryer relative humidity is beneficial. Control of a water streaking defect may be assisted by dipping or spraying at a higher specific gravity.

2.10.12 Reboil

Reboil is due to the evolution of gases from the base metal when it is heated to enamelling temperatures. The greatest evolution of gas occurs in the 600-660°C temperature range. Harder groundcoat firing in order to burn out these gases during groundcoat fire and more fluid groundcoats and covercoats which will allow the gases to

pass and then heal over have been the most successful cures for this type of defect. Obviously, the preferred course is to avoid use of reboiling steels.

2.11 Property Controls

Enamel plant control of milled groundcoats is confined to checking the fineness, specific gravity, set or pick-up, application or spray weight and water content.

Othmer (1961) recommended the following tests of physical and chemical properties of porcelain enamel:

- Adherence
- Thermal expansion fit
- Acid resistance
- Hot water resistance
- Alkali resistance
- Abrasion resistance
- Thermal shock resistance
- Impact resistance
- High gloss
- High reflectance
- Desirable colour
- Flatness of porcelain enamel flatware

CHAPTER THREE

3.0 INSTRUMENTATION AND EQUIPMENT

Various instruments and equipment were used in this research work but only the main equipment set up are described in this section. Other equipment not described in this section are mentioned appropriately in the experimental procedure. The only equipment described in this section is the crucible mould.

3.1 The Crucible Mould

Two types of mould were used - the hump mould made of Cardboard paper is made to the shape and size of the desired crucible. Clay slip for the crucible is draped over the mould and pressed to conform to it.

Plaster of parris (gypsum) mould was used to reproduce crucible shapes. It is made approximately 25 percent larger than the desired final size in order to allow for shrinkage of the crucible during drying and firing.

Figure 4 illustrates the hump mould while Figure 5 is the plaster mould.

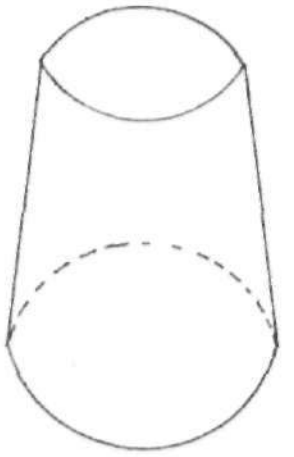


Figure 4: The Hump Mould

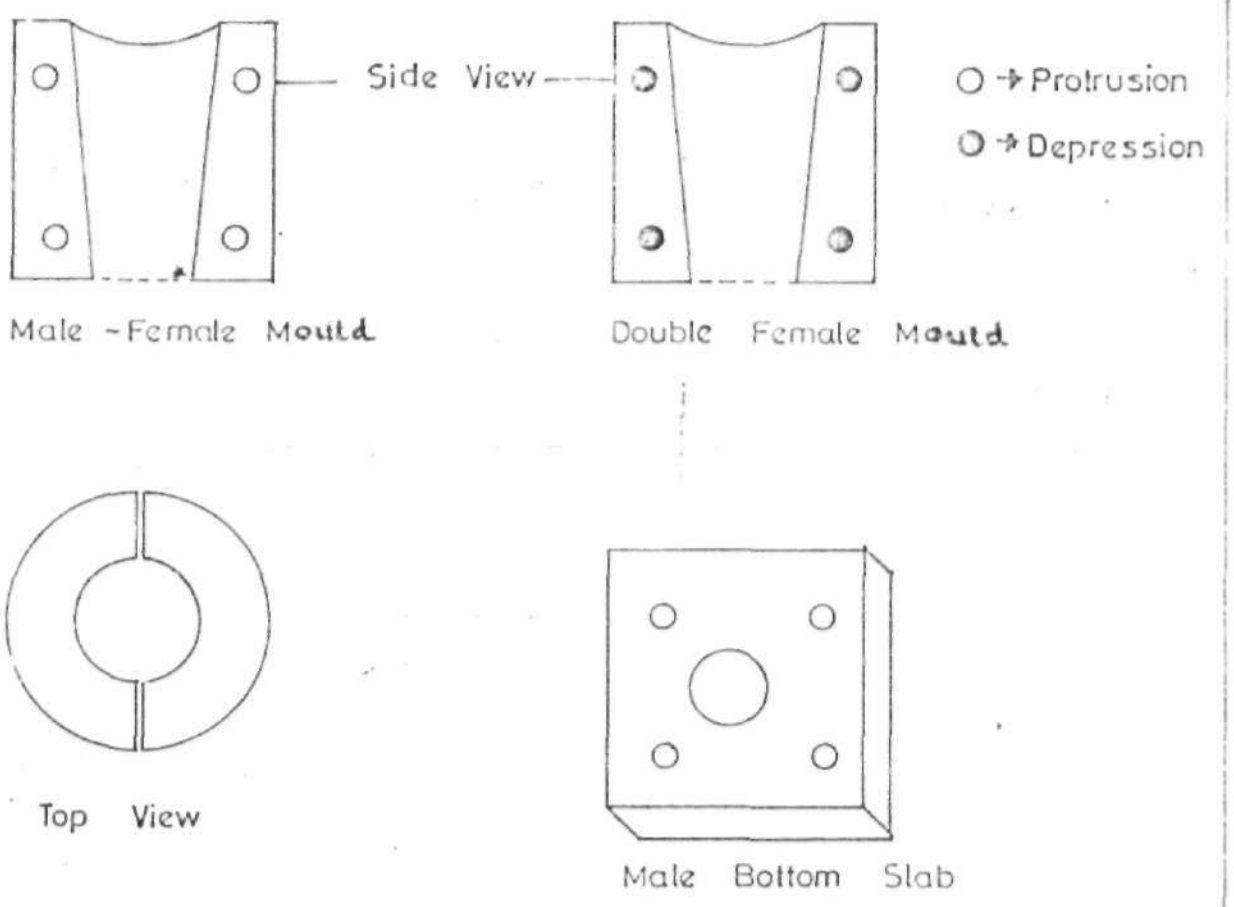


Figure 5: The Plaster of Paris Mould

CHAPTER 4

4.0 EXPERIMENTAL PROCEDURE

The experimental procedure is divided into seven stages: Crucible development and production; body preparation; enamel proportioning, smelting and fritting; mill room operations; metal preparation; enameling operation and quality control tests. Each of these operations is described in this chapter.

4.1 Crucible Development and Production

In the course of carrying out this research work, the problem posed by inavailability of fireclay crucibles was so crippling that it was necessary to develope and produce the fireclay crucibles used in this work. Moreso the enamel ingredients attacked and damaged other crucibles like Nickel crucibles used in initial experimental trials. The initial crucibles were produced using hump mould method. The need for a uniform size and shape of crucibles led to the use of plaster of paris mould.

4.2 Body Preparation

The clay and grog were screened using a 30-mesh (590 microns) sieve for best particle size and to separate the too coarse particles. This screening was necessary to minimize the porosity of the crucible. Too coarse particles

do not produce the desired plasticity and workability in the clay.

Using Armfield sensitive gram - weighing balance, 70 percent raw clay (Kankara kaolin) was weighed into a V-blender with 30 percent calcined clay (grog). Grog was used for the crucible body because it acts to open up the clay body for more uniform drying. The grog also minimizes shrinkage and the subsequent cracking of the crucible.

Even clays from the same bed will vary slightly in chemical and physical qualities. Thus the clay and grog were mixed dry in the V-blender in order to achieve a uniform and workable body. The mixture from the V-blender was poured into a bath and enough water added for the wet mixing which brought about the plasticity of the clay body. The wet body was wedged and kneaded to obtain a uniform consistency. The wedging and kneading is also responsible for the removal of air bubbles from the clay slip.

Two moulding methods were used. In the hump mould method, a carboard mould of the shape and size of the desired crucible was used to form the crucibles. Plastic clay was pounded and rolled with the head of the hand to the desired thickness in the bath floor. The resulting slab was then draped over the mould and pressed to conform to it. The excess clay was trimmed off. Care was taken to use only the right amount of clay as too much of it resulted in unduely thick and heavy crucible while too little resulted in thin, light and collapsible crucible that was too fragile

after firing. Moistened paper towel was shaped smoothly over the mould before the clay application. The crucible formed after drying slightly and was removed without sticking.

In the plaster of paris mould method, the clay-grog mixture was mixed with water to a consistency of syrup (casting slip). Dried P.O.P. moulds were filled with casting slip. The material remained in the mould from 2 to 8 minutes and then the excess slip was removed from the mould by pouring it out (drain casting). The result of this operation is a uniform coating of slip inside the mould. The slip coating became firm and strong and gradually seperated from the mould as it dried. It was then freely removed from the mould the crucibles formed by any of the methods were carefully dried in an electric oven. When the crucibles were thoroughly dried out, they were subjected to the first or bisque firing in the electric furnace.

The crucibles were fired to 1200^{o}C and soaked at this temperature for upwards of two hours. The fired crucibles were then removed and allowed to cool. The 1200^{o}C temperature is the maximum temperature of the furnace and hence constrained further heating. The operational sequence for the crucible production is shown in Figure 6.

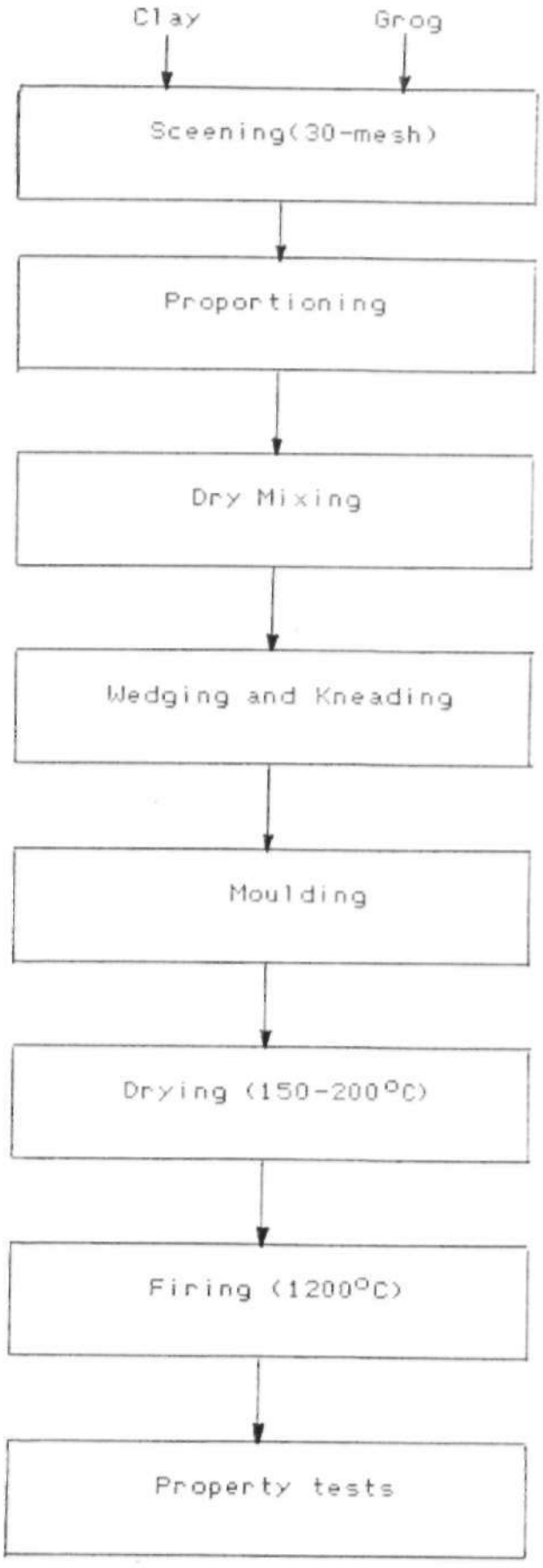


Figure 6: Operation Sequence for Crucible Production

4.3 Enamel Proportioning, Smelting and Fritting

The basic ingredients of all the enamel formulations were made up primarily of inorganic chemical compounds and minerals. The use of refined chemicals which are mostly imported was reduced to the barest minimum. Materials used were mostly those minerals with proven abundant reserve in the country in their relatively pure state.

In this work, several formulations were prepared. The qualities imparted to the enamel by the different ingredients were best understood by making several formulations with varying proportions of these ingredients. Triaxial diagram for quartz, feldspar and flux as illustrated by Figure 7 was used as an easier and more organised proportioning system. By using this triaxial diagram, considerable effort and time was saved by concentrating on those areas where meaningful results were expected. Clay was used in place of quartz in the formula where additional alumina was to be supplied other than that supplied by feldspar. Many fluxes were used in the formulations and had the advantage of extending the firing range of the enamel and enchanced more complete fusion of the ingredients with emergent fewer enamel defects. Table 12 is summary of batch enamel formulations while Table 13 is the corresponding oxide formulae. Detailed calculations of oxide formulae are presented in Appendix E.

The ingredients were correctly weighed using a very sensitive Armfield gram-weighing balance and thoroughly *mixed in the V-blender before smelting.* The thoroughly miced enamel ingredients were placed in the fireclay crucibles and smelted in an Armfield box type electric furnace according to the smelting schedule in Figure 8.

Decomposition, gas evolution and solution of the ingredients occured during smelting. After the molten glass was smelted to a uniform and homogeneous liquid, which took from 1.5 hours to 3 hours of more, the crucible was withdrawn from the furnace using tongs and the molten liquid was quenched by pouring in a thin stream into bath of water. This is called quenching. This quenching shattered the whole mass into tiny fragments called frits. The frits were removed from the water and dried.

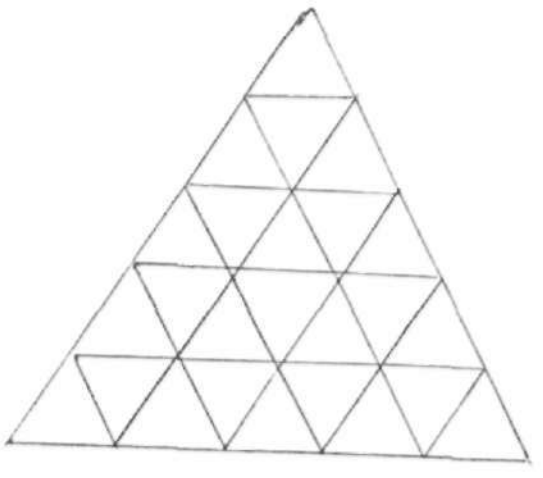


Figure 7: Triaxial Diagram for Enamel Blending

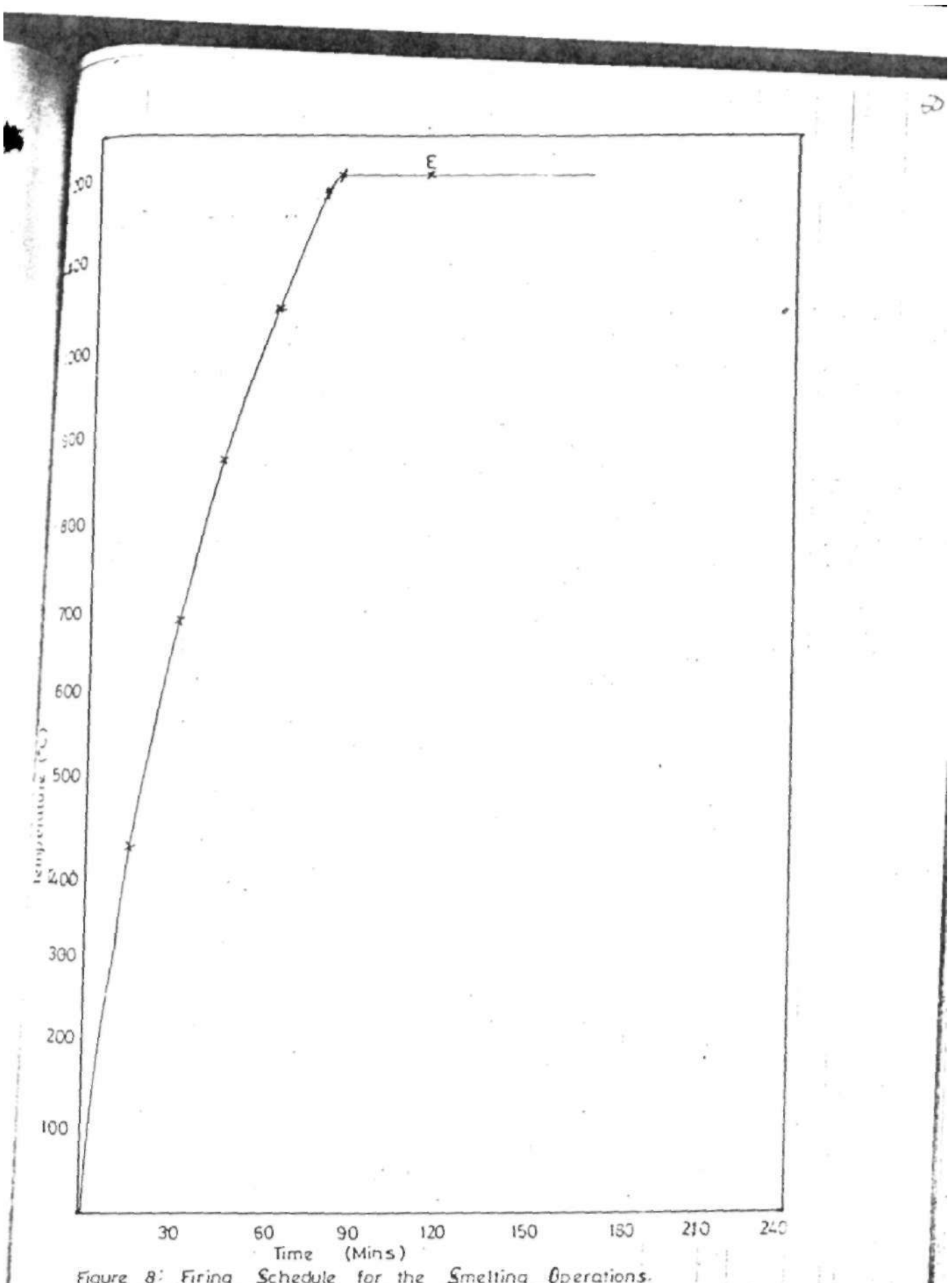


Figure 8: Firing Schedule for the Smelting Operations.

Table 12: Summary of Batch Enamel Formulations

Material	Weight Percentages				
	A	B	C	D	E
Feldspar	32	30	35	25	25
Quartz	20	26	23	25	25
Kaolin	-	-	-	10	-
Boric Acid	20	18	18	15	20
Fluorspar	20	-	8.0	-	8.0
Salt Petre	-	1.0	1.5	2.0	-
Magnesite	2.5	5.0	-	6.0	-
Whiting	5.0	5.0	-	4.0	1.5
Soda Ash	4.0	4.0	7.0	3.0	8.0
Soda Nitre	3.0	2.0	6.0	2.0	6.0
Barium Carbonate	5.0	3.5	-	3.0	-
Salt	-	1.0	-	1.0	-
Cobalt Nitrate	0.5	1.0	1.0	1.5	1.0
Manganese Dioxide	2.0	3.0	0.5	2.0	4.5
Nickel Carbonate	1.0	0.5	-	0.5	1.0

Table 13: Summary of Oxide Enamel Formulations

Oxide	Oxide Percentages in Formulations				
	A	B	C	D	E
K_2O	5.9	8.7	7.5	4.6	4.8
Na_2O	3.8	0.6	7.0	3.9	7.9
CaO	10.5	9.3	7.5	5.2	9.4
MgO	1.3	3.8	-	3.1	0.01
Fe_2O_3	0.08	0.1	0.1	0.3	0.1
B_2O_3	13.7	10.0	12.5	10.1	14.2
Al_2O3	7.3	6.9	8.1	9.1	5.9
SiO_2	49.8	58.9	56	56.3	51.9
MnO_2	2.0	0.9	0.5	1.9	4.6
BaO	4.7	-	-	4.6	-
CoO	0.2	0.4	0.4	0.5	0.3
NiO	0.8	0.4	-	0.4	0.8

4.4 Mill Room Operations

The mill room practice involved grinding of the frit and screening, proportioning of the mill batch, property quality control of the milled batch and storage.

Motar and pestle was used in the grinding operation because of the small quantity of frit batches. The only diadvantage of mortar and pestle was the excess time and manpower required to reduce the frits to desired particle size. Dry grinding was used. The fineness of griding of enamel batch was tested by screening. 4-8 percent residue on 200 mesh (74 microns) was ideal. Coarse particles were returned for regrinding.

Materials were added in the following order: electrolytes, clay, gum frit and then water. The materials were thoroughly mixed in the beaker with the glass rod. The control of the milled groundcoats was confined to checking the following properties: milling or grinding fineness, specific gravity, pickup, application weight and water content. The milled enamel was allowed to age for 8-24 hours before use. Aging allowed the softening and cooling of the enamel and the escape of entrapped air. The milled enamel was stored in the glass beaker and occasionally stirred to discourage seperation of the enamel slip.

4.5 Metal Preparation

The metal preparation operation involved the following processes: sheet cutting, annealing, smoothening, alkali bath, pickling, nickel dip and neutralizing as illustrated in Figure 9.

4.5.1 Sheet cutting

The steel sheet was cut into convinient sizes and shapes using a pair of metal shears. Pieces in the size of 30mmx40mm to 45mmx50mm were mainly used. The steel sheet was marked out into the desired sizes and shapes using metal ruler and scribber. Shear blades were kept sharp to ensure smooth cutting.

4.5.2 Burning off or annealing

This was only used for steel stock with excess greases and oil which could not be removed by ordinary cleaning methods. The piece was placed in the furnace at 660-720°C and heated until all the oil or grease was burnt off. This operation required from 1-3 minutes or longer depending on the amount and type of oil or grease covering the piece.

4.5.3 Smoothening

Steel sheets of 14 gauge or heavier were smoothened without fear of warpage, sagging or other defects characteristics of lighter gauges. This smoothening was

done by the use of emery cloth. The files were used to smoothen out sharp edges. The flat faces of the steel pieces were smoothed out on the anvil using the mallet. Occasionally, grinding wheels were used to file out rough edges and surfaces.

4.5.4 Alkali bath

Smoothening does not remove grease or oil that has been absorbed into the metal. This absorbed oil or grease was removed by soaking the steel pieces in an alkali bath. The alkali bath also removed organic contaminants. The alkali solution was made up of 5 parts caustic soda, 5 parts sodium sulphate and 10 parts detergent in water. When the piece was removed from this solution, it was rinsed in hot water at a temperature of 82-93°C for 3 minutes.

4.5.5 Picking or acid bath

The pickling solution contained 11 percent hydrochloric acid and the solution was kept at room temperature. Occasionally, 6 percent sulfuric acid heated to a temperature of 80-85° was used.

Pickling removed oxidized metal, reduced discoloration and soiling and enhanced metal softening. The pickling process lasted for about 15-25 minutes or as long as it was necessary to remove the scales. After pickling, the pieces were rinsed in a hot water bath at a temperature of 82-88°C for 3 minutes.

4.5.6 Nickel dip

The nickel dip solution contained 16 parts nickel sulphate, 1 part boric acid, 1 part ammonium carbonate and water. The nickel - dip process gave a better bond to the steel and groundcoat. The solution was used at a temperature of 70-88°C. The metal pieces were immersed in the solution for a period of 5-10 minutes. The steel pieces were removed from this nickel solution to a hot or cold water bath for 1 minute or less.

4.5.7 Neutralizing bath

The neutralizing solution was made up of 4 percent of alkali made up of soda ash, trisodium phosphate and water. This bath was heated to a temperature or 80°C for maximum efficiency. After the steel pieces were removed from the neutralizing solution, they were immediately dried at a temperature of 120°C in the oven. The pieces were then gauged for thickness before enamel application.

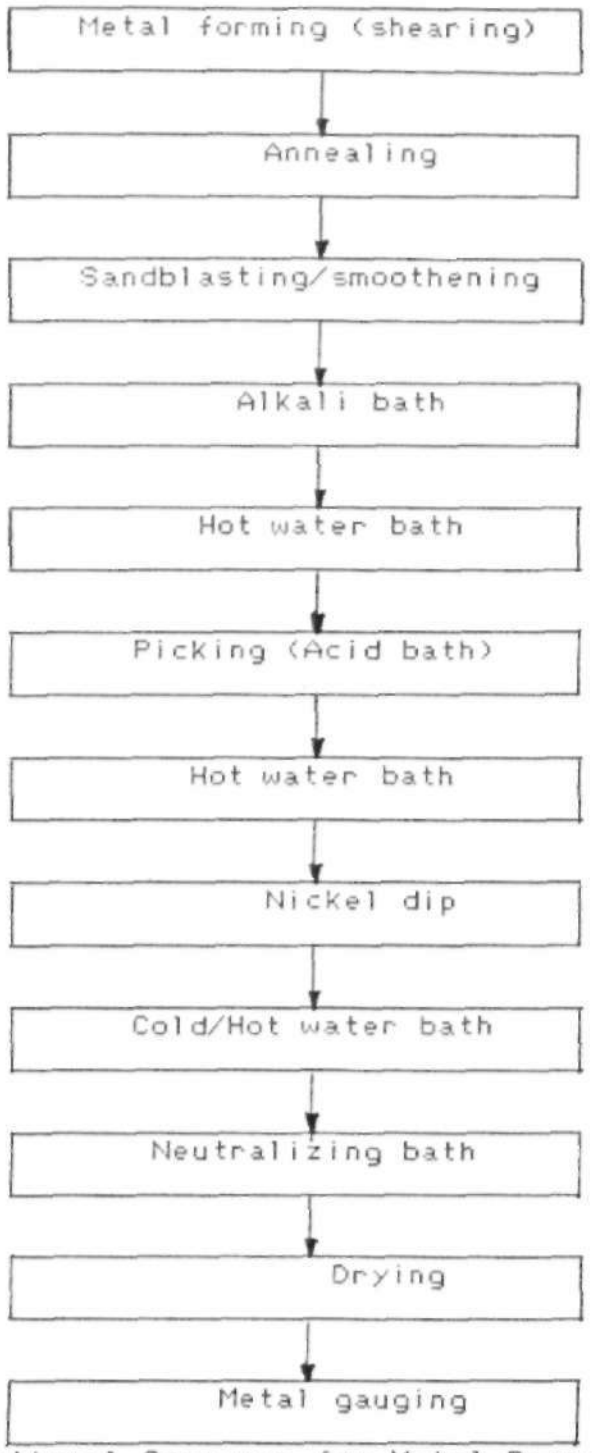


Figure 9: Operational Sequence for Metal Preparation

4.6 Enameling Operation

The enamelling operation involved enamel application, drying and firing.

Liquid enamel (slip) was applied by dipping the steel piece in the slip with the pair of tongs and allowing the excess to drain off. Care was taken to ensure that the enamel slip drained evenly and uniformly without drain streaks and as repidly as possible. The slip was prepared to have enough set to permit a desired weight of coating to remain on the piece after draining. Dipping was found more economical than any other method of application since all sides of the test piece was coated in one operation. Also dipping ensured that the resultant coating was uniform and free of bubbles or other defects.

After the enamel slip had stopped draining and was "set" pieces were placed on trivets placed at the 'hearth' of the furnace. With the furnace maintained at 150^{o}C, the pieces were dried for $1^{1}/2$ - $2^{1}/2$ minutes. Complete drying was necessary before the piece was fired. A crusty feel to the touch indicated complete drying.

With the trivet still in place in the furnace the furnace was heated to the maturing temperature range of the enamel. When this temperature was attained, the furnace door was opened and with the pair of tongs, the bisque fired test piece was placed on the trivet as quickly as possible without disturing the enamel. The furnace door was immediately closed to minimize heat losses. When the piece had fired for about 2-3 minutes, the furnace door was opened

slightly for an instant to observe the firing process. When the piece became bright red and the enamel appeared shiny and nearly smooth, it was withdrawn from the furnace with the pair of tongs. It was cooled at room temperature. The firing or burning process took between 3 and 15 minutes depending on the enamel and the firing temperature. The firing temperatures for the samples varied from 830°C to 920°C.

4.7 Quality Control Tests

In assessing the quality of the finished enamel piece, standard methods of testing recommended by the Nigerian Standard Organisation (Nid: 48(1974) was used. The standard covered enamelware having steel as the base metal. This standard is currently used by all enamelware industries in the country. The tests covered include coating thickness, quench or thermal shock test, acid resistance, impact resistance and finish.

4.7.1 Metal/coating thickness

The thickness of the metal and the coating thickness were measured by means of a micrometer screw gauge at five points in the test piece; each point was at a distance of about 10mm or less from the former one depending on the size of the test piece. The average of such measurements was taken as the thickness of the metal or coating. The overall (metal + coating) thickness minus the metal thickness gave the coating thickness.

4.7.2 Quench or thermal shock test

The test enamelled pieces from each enamel formula were heated in the oven so that a steady temperature of 185°C to 195°C was reached in about 10 minutes. The samples were quenched in a bath of water at room temperature. They were dried and the heating and quenching was repeated eight times. Heating for each cycle was carried out at progressively higher temperature. The temperatures used were 170, 175, 180, 185, 190, 195, 200 and 205 successively. After undergoing eight cycles of test, the samples were examined for possible signs of crazing, flaking off or cracking.

4.7.3 Acid resistance test

The test consisted of a 15 minutes exposure of the test piece to a 10 percent solution of citric acid and evaluation of the effects in terms of damage in appearance and relative cleanability of the surface resulting from the test.

The test piece was washed with warm 1 percent trisodium phosphate solution, rinsed in warm water and then cleaned with soft towel. The test piece was placed in the 10 percent citric acid solution at room temperature and after about 15 minutes of treatment, it was removed, rinsed in water and dried with a clean soft towel by blotting (not rubbing). The grading was done 2 hours after the test.

The grading was of three categories as illustrated in Figure 10 from the Figure A1 and A2 were the passing grades. A1 passed dry-rubbing test and had no stain. A2 passed

wet-rubbing and blurring highlight tests. B2 failed wet-rubbing test and passed blurring-highlight test.

In the visual examination, the test piece was viewed at various angles with respect to the light source and the eye so as to detect the difference between the surface and that of untreated piece. Daylight made available within a few metre of an outside window was used.

In the blurring-highlight test, a desk lamp with an incandescent bulb was used. The test piece was held so that the image of the lamp bulb was observed as a high-light in the test piece, the line of vision being within 45° to the surface. The eyes were focussed on the image of the light source and the test piece was shifted to bring this image into the test piece. Any colour difference in the enamel due to staining was ignored. The test piece failed the test if a definite blurring of the image was observed.

In the dry-rubbing test, four parallel lines were drawn with the flat point drafting HB pencil on the test piece. The lines were drawn with firm pressure. The surface was rubbed across the lines repeatedly with dry, clean soft, cotton towel in the direction shown in Figure 10. The test piece passed the rubbing test if the marks were completely removed from the test piece.

In the wet rubbing test, the same operation as in the dry rubbing test was carried out with a new treated test piece. A clean, soft, cotton towel was dipped in water and wrang and then used to rub the pencil mark. The piece passed the test if all the pencil marks were completely removed.

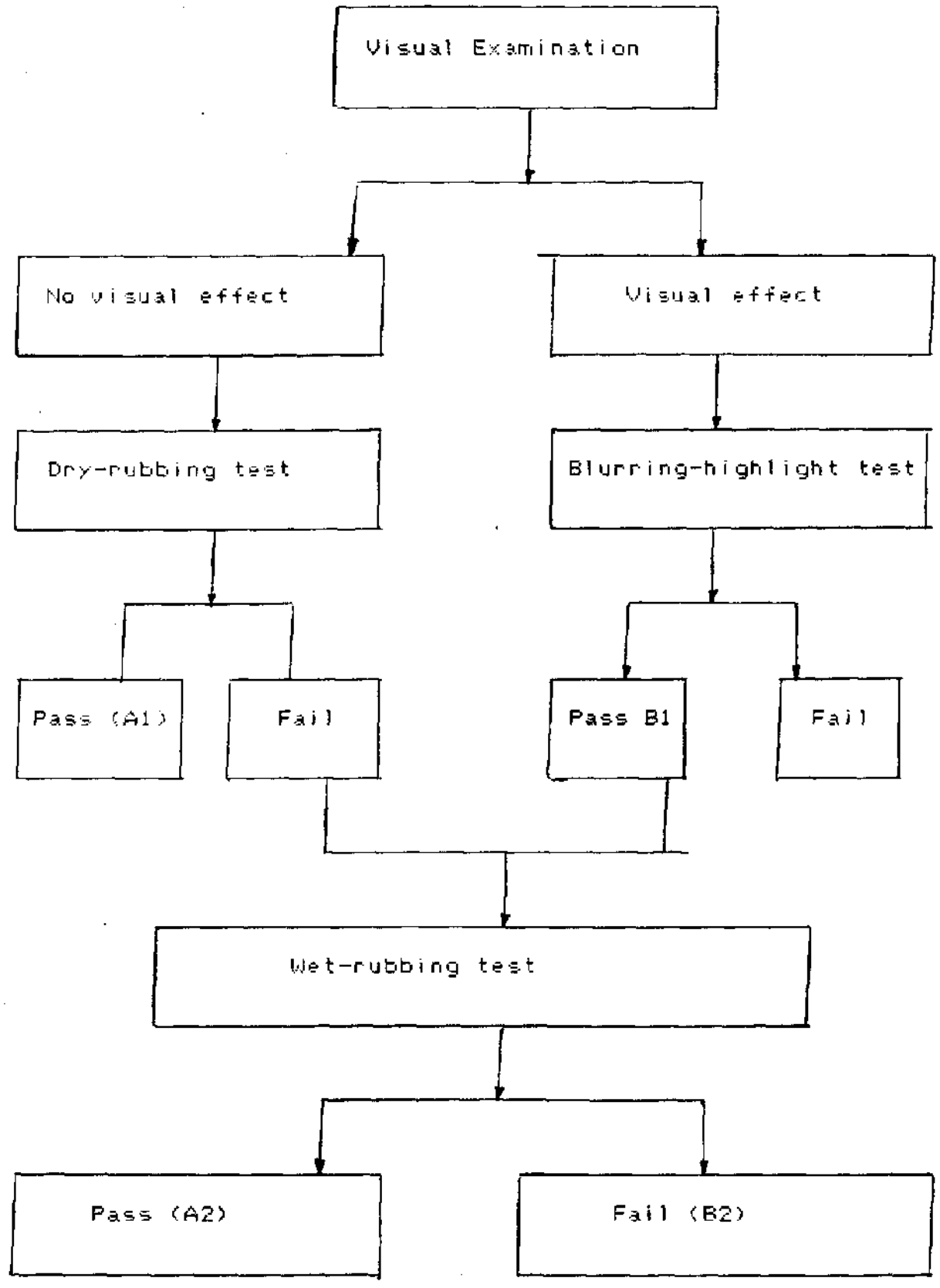


Figure 10: Acid Resistance Test Grading Scheme

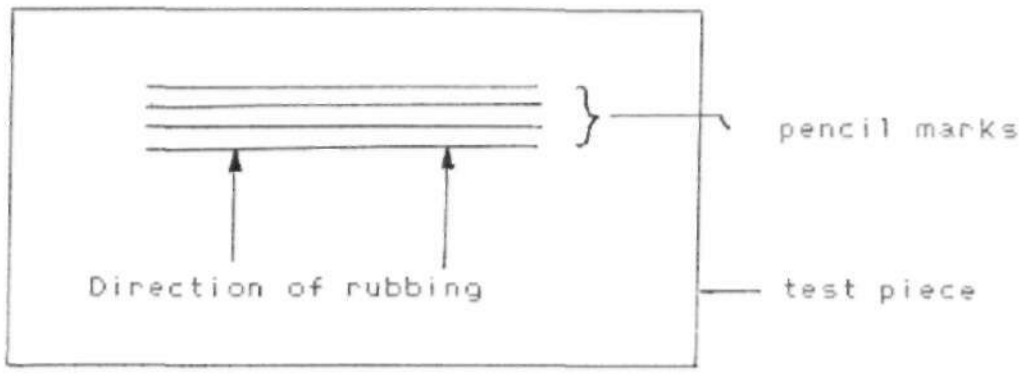


Figure 11: Rubbing Direction of the Rubbing Test

4.7.4 Impact resistance test

This test was carried out at ten different points of the test piece. A steel ball of 100g was allowed to fall on the enamel coating from a height of 565mm. The ball was allowed to fall on ten different points of the test piece. The piece passed the test if there was no resultant damage to the enamel coating.

4.7.5 Finish or gloss test

The enamelled piece was tested for noticable warpage, uniformity of coating, completeness of covering, spots of bare base metal, cracks pin-holes or crevices by visual inspection. The pieces were also inspected for desired colour, texture and gloss.

CHAPTER FIVE

5.0 RESULTS AND DISCUSSION

The results of this research work are presented in this chapter.

5.1 *Proportioning, Smelting and Fritting*

Many formulations were smelted but only the five that yielded best performance properties are dicussed.

Enamel B had the highest local input of 84 percent, followed closely by D with 78 percent local input, then A with 71.5 percent, C with 68 percent and E with 64 percent. A, C, D and E showed ductile behaviour of the smelted mass and shattered into small particles during quenching while B was brittle and formed lumps on quenching. The fusion (maturing) temperature increased with increase in clay or quartz and decreased with increase in flux content. Enamel E had the lowest maturing temperature of 1080°C, followed by A with maturing temperature of 1115°C, C and D had maturing temperature of 1150°C while B matured at 1200°C. Complete smelting of the masses was attained after about 1.5 hours to 3 hours. Salt petre (Potasium nitrate) added in some batches caused excessive foaming especially in formula B though it reduced drastically the smelting time. Table 14 summarizes the local material content, smelting temperature and time of the batches. Feasible region for sheet steel

groundcoat enamel formulations is presented in Figure A1 of Appendix A while enamel raw materials and their functions is presented in Appendix B.

Table 14:Summary of Local Raw Material Content, Smelting Time and Temperature of the Formulations

Formula	Local Raw Material Content (%)	Maturing Temp.(°)	Maturing Time (mins)
A	71.5	1115	150
B	84	1200	90
C	68	1150	105
D	78	1150	180
E	64	1080	120

5.2 Enamel Slip Preparation

One disadvantage of the laboratory enamelling practice was the extremely long grinding time necessary to pulverise the frit to adequete fineness using pestle and mortar. Though enamels A, C, D and E were friable and proved less difficult in grinding, B was very hard and proved very tough on grinding.

4-8 grams residue on 200 mesh from 100g sample attained after continuous grinding, secreening and regrinding gave good results. Better results were obtained using laboratory ball mil. Grinding below this limit resulted to tearing in

the enameled piece while too coarse particles gave rough surface characterised by copperheads. Aging for 24 hours produced a soft slip that uniformly covered the metal surface during dipping. 0.5 ~ 1g of clay per 10g of frit gave best fit to the bisque body while 0.3-0.5g electrolytes per 10g frit gave most successful results duringd firing. The addition of enamelling gum did not give any additional performance property in the final finish rather it deteriorated the enamel slip after standing for 48 hours. Table 15 summarised the mill additions used in the various formulations and for various mixes. Ikebedi clay which is very plastic was used in the mill additons.

Table 15: Mill Additions Used

Slip MIx	Frit(g)	Enamelling Gum (g)	Sodium Nitrate (g)	Magnesium Carbonate (g)	Clay (g)
A1	5	-	-	0.5	0.50
A2	5	0.2	0.5	-	0.30
A3	5	-	0.5	-	0.30
A4	5	-	0.25	0.25	0.20
A5	10	0.5	0.8	-	0.30
B1	10	-	0.8	-	0.30
B2	10	-	4.4	-	0.80
B3	10	-	-	0.5	0.50
C1	10	-	0.5	-	0.50
C2	10	0.1	-	2.0	0.50
C3	10	-	1.0	-	0.20
D1	10	-	0.3	-	0.75
D2	10	-	0.4	-	0.50
D3	10	-	0.5	-	1.00
E1	10	-	0.4	-	1.00
E2	10	-	0.35	-	1.20
E3	10	0.2	1.0	-	0.50
E4	10	-	0.45	-	0.75

5.3 Metal Treatment

Physical metal treatment which involved sheet cutting/ annealing, sandblasting and smoothening in most cases gave better and cleaner surface that produced better bond than most chemically treated ones.

Pickling with 6 percent sulfuric acid at 80-85°C gave a cleaner surface than pickling with hydrochloric acid (11 percent) at room temperature. Pickling with sulfuric acid was also faster. Metal pieces treated with Nickel solution produced better bond than those that passed through ordinary acid pickling. The longer the nickel dipping the better was the bond.

Neutralizing for 24 hours at room temperature gave better result than for a very short time at 70-88°C.

5.4 Enameling Operation

Aged enamel slip gave smooth and uniform coating on dipping and draining. A very thick consistency of the slip also assumed complete coverage of the metal surface in a single drain. However, the thicker the consistency of the slip, the higher the coating thickness (application weight) and the higher the risk of peeling in the fired body. 30-40 percent water content gave best result for dipping. Physically treated metal pieces required thicker consistency because of its streaking tendencies than the chemically treated ones. Drying at 150°C for 1.5 - 2.5 minutes gave better results than at a higher temperature for shorter time. Drying at a higher temperature for a shorter time

produced chalking effect. The firing schedule for the formulations and mixes are presented in Tables A1-A5 of Appendix C. The firing temperature somehow followed the same trend as the smelting temperature. Optimum firing schedule for the optimum slip for all the formulations is presented in Table 16. The optimum slip was adopted from Table 15.

Table 16: Optimum Firing Schedule for the Formulations

Formula	Optimum Slip	Optimum Firing Temp. (^{o}C)	Optimum Firing Time (mins)
A	A1	845-870	5-10
B	B2,B3	870-880	8-10
C	C1	850-860	8-10
D	D1,D2,D3	850-875	6-12
E	E1,E2,E4	840-855	4-8

5.5 Quality Control Tests

The results of the quality control tests which included metal and coating thickness, quench or thermal shock test, acid resistance, impact resistance and gloss or finish are herein presented.

5.5.1 Metal and coating thickness

Only metal pieces that were chemically treated without sandblasting were selected for the purpose of determining the metal thickness. The metal thickness (gauge) were determined for these pieces and found to be the same for all chemically treated pieces from the same stock without sandblasting. This uniformity advantage was taken to determine the, thickness of the coating. The result of five sample test pieces are presented in Table 17. The metal has a uniform thickness of 0.95mm while the coating thickness varied from 0.40mm-0.48mm. The metal thickness for physically treated pieces varied significantly according to the degree of sandblasting involved. An average thickness of 0.75mm to 0.88mm being most common. The chemically treated metal for this test was taken from the same batch as metal thickness depended on the amount of etching involved.

Table 17: Metal and Coating Thickness

Metal Piece	1	2	3	4	5
Metal Guage (mm)	0.95	0.95	0.95	0.95	0.95
Point 'a' Guage (mm)	1.36	1.42	1.38	1.47	1.35
Point 'b' Guage (mm)	1.32	1.39	1.36	1.43	1.32
Point 'c' Guage (mm)	1.38	1.41	1.40	1.46	1.34
Point 'd' Guage (mm)	1.35	1.37	1.41	1.40	1.38
Point 'e' Guage (mm)	1.40	1.35	1.45	1.38	1.38
Average Guage (mm)	1.36	1.39	1.40	1.43	1.35
Coating Thickness (mm)	0.41	0.44	0.45	0.48	0.40

5.5.2 Quench or thermal shock

All the formulations passed the thermal shock test as no visible signs of crazing, flaking off or cracking was observed after eight successive cycles of heating and quenching. The result of the test is presented in Table 18.

Table 18: Quench or Thermal Shock

Test Piece	Observation at Test Temperatures (°C)							
	175	180	185	190	195	200	205	210
A1	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
A2	"	"	"	"	"	"	"	"
A3	"	"	"	"	"	"	"	"
B1	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
B2	"	"	"	"	"	"	"	"
B3	"	"	"	"	"	"	"	"
C1	Nil	Nil	NIl	Nil	Nil	Nil	Nil	Nil
C2	"	"	"	"	"	"	"	"
C3	"	"	"	"	"	"	"	"
D1	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
D2	"	"	"	"	"	"	"	"
D3	"	"	"	"	"	"	"	"
E1	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
E2	"	"	"	"	"	"	"	"
E3	"	"	"	"	"	"	"	"

5.5.3 Acid resistance

The result of the acid resistance tests is presented in Table 19. Enamels B,D and E passed the visual and dry rubbing test outright. Enamels A and C showed a significant damage in appearance after immersion in citric acid solution. However the blurring highlight test conducted on these A and C samples could not be relied upon for lack of precision in carrying out the test. The two enamel samples passed the blurring highlight test and failed the wet rubbing test.

Table 19: Acid Resistance

Test Piece	Visual Test	Dry-Rubbing Test	Blurring Highlight Test	Wet-Rubbing Test
A1	Fail	-	Pass	Fail
A2	Fail	-	Pass	Fail
B1	Pass	Pass	-	-
B2	Pass	Pass	-	-
C1	Fail	-	Pass	Fail
C2	Fail	-	Pass	Fail
D1	Pass	Pass	-	-
D2	Pass	Pass	-	-
E1	Pass	Pass	-	-
E2	Pass	Pass	-	-

5.5.4 Impact resistance

All the enamels passed the impact resistance test as cracks and peeling off were absent in all the samples.

5.5.5 Finish or gloss

Enamel E had the highest gloss and desired colour. The order of gloss and desired colour is E> A> D> C> B. No warpage was noticed.

When compared with industrial samples I1 and I2 their performance properties are as summarised in Table 20 while Plate I is a picture of all the formulation as applied along with the imported industrial stocks. The samples are arranged in rows in the order A, B, C, D, E, I1 and I2.

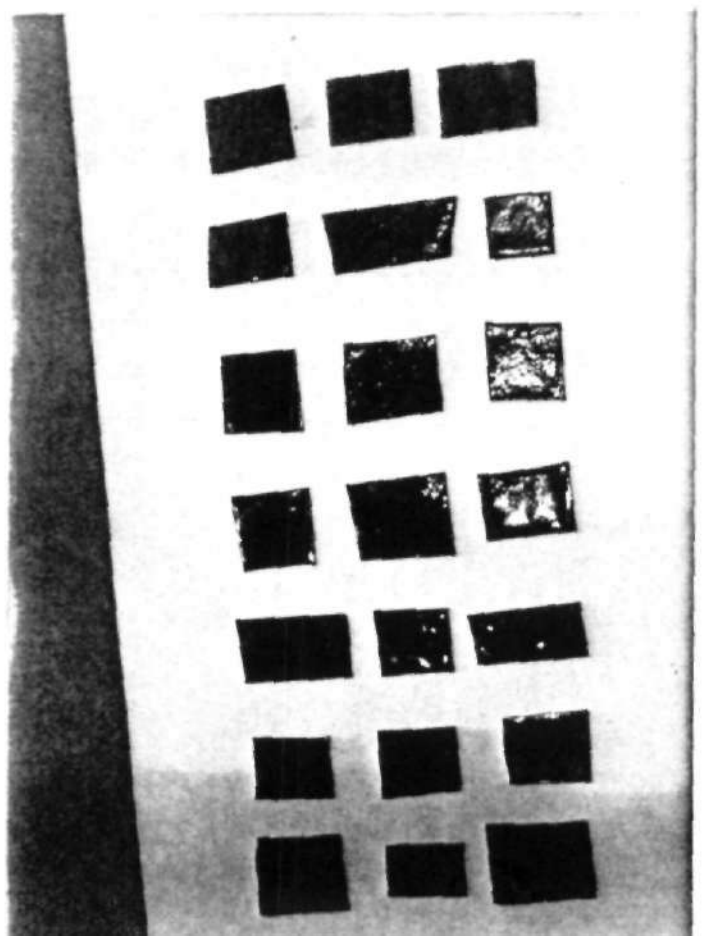


Table 20: Comparative Qualities of Developed Enamels and the Imported Industrial Stock

Enamel	Adherence to Metal	Acid Resis- Tance	Impact Resis- tance	Thermal Stock Resis- tance	Gloss	Desi- rable colour	Remarks
A	Good	Fair	Good	Good	High	Good	
B	Good	Good	Good	Good	Low	Fairly Good	Copper heads present
C	Fairly Good	Fair	Good	Good	High	Good	
D	Good	Good	Good	Good	Low	Fair	Slight discolo ration
E	Good	Good	Good	Good	High	Good	
I1	Good	Good	Good	Good	High	Good	
I2	Good	Good	Good	Good	High	Poor	High discolo ration

CHAPTER SIX

6.0 CONCLUSION

Based on the results of this investigation, the following conclusion can be made.

1. Of the five formulations that yielded best perfomance properties, enamel B had the highest local input of raw materials (84 percent), followed closely by D with 78 percent, then A with 71.5 percent, C with 68 percent and finally E with 64 percent.

2. Enamel E had the lowest maturing temperature of 1080^{o}C, followed by A with maturing temperature of 1115^{o}, C and D had 1150^{o}C maturing temperature while B matured at 1200^{o}C. Complete smelting of the masses was attained after 11/2 to 3 hours.

3. Enamel frits A, C, D and E were friable and proved less difficult in grinding while B was very hard and proved very tough on grinding. Ball milling gave better results.

4. Pickling with 6 percent sulfuric acid at 80-85^{o}C gave a cleaner surface than pickling with hydrochloric acid (11 percent) at room temperature. Also pickling with sulfuric acid was faster. Metal pieces treated with nickel solution produced better bond than those that passed through ordinary acid pickling.

5. Drying the enameled piece at 150°C for 11/2 -21/2 minutes gave better result than at a higher temperature for shorter time. Drying at a higher temperature for a shorter time produced chalking effect.

6. Enamel E had the lowest firing range of 840 - 855°C with firing time of 4 - 8 minutes. Enamel A followed with firing range of 845 - 870°C and time of 5-10 minutes. Enamel C had firing temperature of 850-860°C and 8-10 minutes time. Enamel D had 850-875°C firing range and 6-12 minutes firing time while B fired at 870-880°C for 8-10 minutes.

7. All the formulations passed the thermal shock test showing no defect in property after the test.

8. Enamel B, D and E passed the acid resistance test while A and C failed.

9. All the enamels passed the impact resistance test as cracks and peelingg off were absent in all the samples.

10. Enamel E had the best performance properties and compares favourably with the industrial standards I_1 and I_2.

CHAPTER SEVEN

7.0 RECOMMENDATIONS

Based on the results of this investigation, the following recommendations can be made for future work on sheet steel *groundcoat enamels*.

1. In this investigation, only feldspar and clay were used as the only source of alumina. These materials should be substituted using cryolite which have proven abundant reserve in the country and fire at relatively lower temsperature.

2. The total substitution of boric acid or borax with phosphates should be investigated. This substitution will yield about 98 percent raw material sourcing for the enamels as this alone constitutes about 95 percent of the foreign input.

3. An investigation should be carried out on the use of low temperature leadless frits on steel. This would appeal to appliance manufacturers because much lighter guage steel could be used. The heavy guage of steel now used is only necessary because of high temperatures involved and to prevent warping. This is a field worth investigating as there can be time, material and energy savings made on many manufacturing operations.

4. The behaviours of physically and chemically treated metal to coating adherence was contraditory in this investigation. The effect of chemical and physical treatment of metal on coating adherence could be further investigated.

5. The function of salt petre and common salt in the frit ingredient were not fully understood and could be further investigated

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APPENDIX A

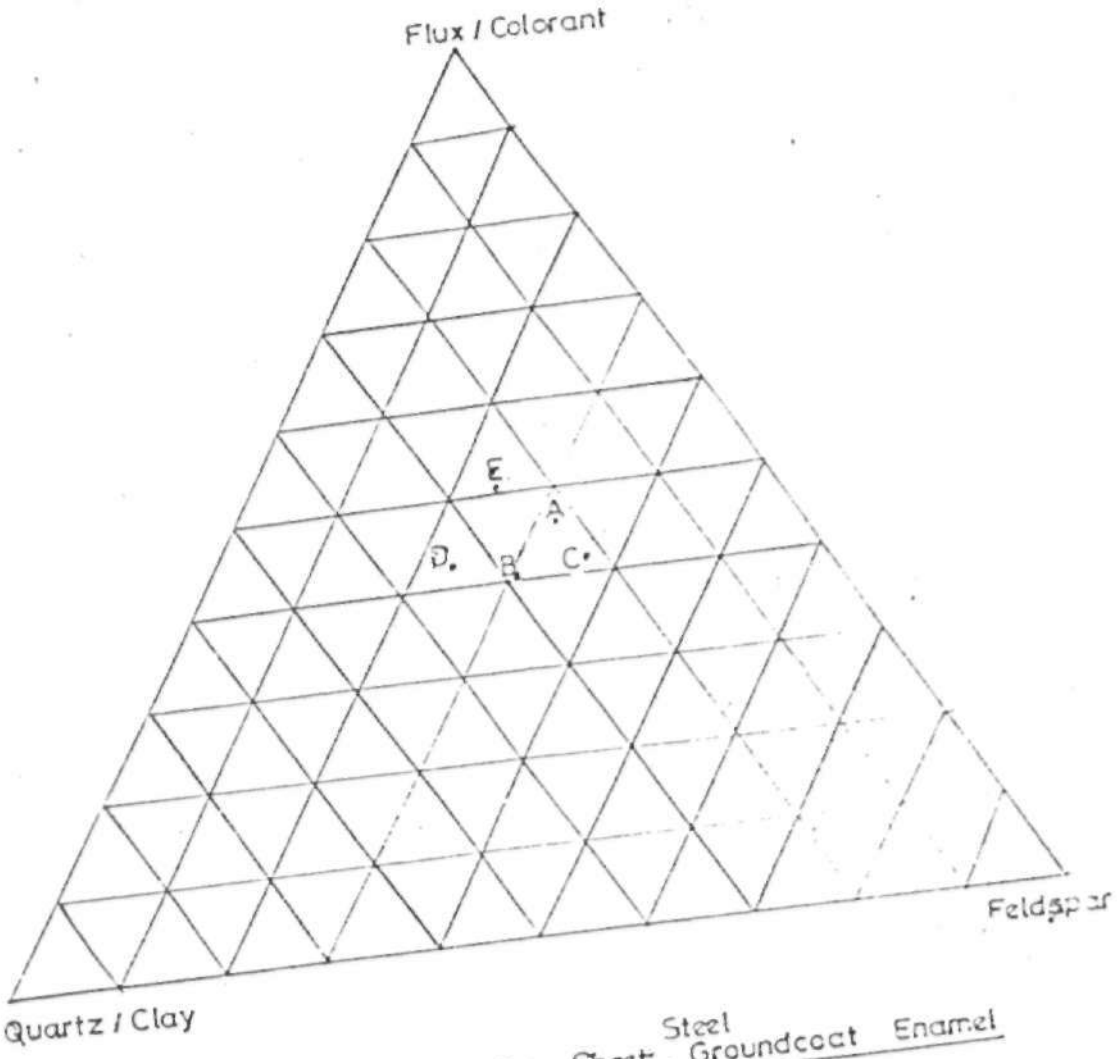


Figure: A1: Feasible Region for Steel Sheet Groundcoat Enamel Formulations.

APPENDIX B

B. ENAMEL RAW MATERIALS

Ammonium Carbonate/Sulphate: Added as a minor ingredient in enamel batches since it is claimed to shorten the melting time and to be more effective than salt cake as an accelerating agent in melting.

Barium Carbonate/Fluoride: Acts as a flux and has the lowest melting point of all the alkaline earth metal. It improves gloss, mechanical strength, elasticity and resistance to organic acid.

Bone Ash: It is characterised by high translucency and whiteness.

Borax/Boric Acid: Flux, imparts important thermal properties necessary to assure proper fit of the enamel to the base metal. It also imparts high luster, strength, toughness and durability and assists in obtaining deep brilliant colourings. It shortens the firing range of most enamels.

Bentonite: Suspending agent for enamel slips.

Caustic Soda: A primary ingredient in cleaning compounds used in the preparation of metal prior to enamelling.

Cobalt Nitrate/Oxide: Disirable for light-coloured first coat enaamel for sheet iron. It is used in groundcoat enamel to give it a tight grip on the metal base.

Clay: Source of silica and alumina in the enamel.

Cryolite: Flux and opacifier. The material is used in amounts up to 15% in white cover coat enamels.

Dolomite: It is used as a flux to supply CaO.,

Feldspar: Source of alumina and silica.

Fluorspar: Flux and opacifier.

Lime (Whiting): A strong flux serving to reduce firing temperature and time and in some cases allowing thinner application.

Magnesium Carbonate (Magnesite): Auxiliary flux end is used as electrolyte in mill batch.

Nickel Oxides: Colorants. It is used in groundcoat alongside with cobalt and manganese.

Potassium Carbonate (Pearl ash): Provides K_2O. It tends to produce high brilliance but it decreases strength and elasticity, making the enamel soft.

Potasium Nitrate (Salt Petre): Has oxidizing and fluxing value,

Quartz: Source of silica

Sodium Carbonate (soda ash): Flux and a source of soda

Salt (sodium chloride): An accelerating agent in melting.

Sodium Nitrate (soda niter): It is used to prevent reduction of any easily reducible ingredient.

Sodium Nitrite - Mill addition to groundcoats to prevent rusting while drying and as a setting up agent.

APPENDIX C

C. FIRING SCHEDULE FOR THE FORMULATIONS

Table A1 Firing Schedule for Enamel A

Slip Mix	Firing Temp. (°C) and Time (min) for Test Pieces									
	1		2		3		4		5	
	Temp	Time	Temp	Time	Temp	Time	Temp	Time	Temp	Time
A1	845	10	860	10	870	5	-	-	-	-
A2	845	12	845	15	880	5	-	-	-	-
A3	880	5	850	8	870	10	-	-	-	-
A4	900	3	920	3	880	4	-	-	-	-
A5	870	6	870	6	880	5	880	5	880	5

Table A2: Firing Schedule for Enamel B

	Firing Temp. (°C) and Time (min) for Test Pieces									
	1		2		3		4		5	
Slip Mix	Temp	Time	Temp	Time	Temp	Time	Temp	Time	Temp	Time
B1	870	7	850	12	840	12	880	10	840	15
B2	850	6	860	5	920	4	850	12	870	10
B3	870	8	860	10	880	10	900	5	900	4

Table A3: Firing Schedule for Enamel C

	Firing Temp. (°C) and Time (min) for Test Pieces									
	1		2		3		4		5	
Slip Mix	Temp	Time	Temp	Time	Temp	Time	Temp	Time	Temp	Time
C1	860	8	860	10	850	10	880	6	850	8
C2	900	4	900	3	880	12	860	5	870	5
C3	860	7	860	8	870	8	880	8	900	6

Table A4: Firing Schedule for Enamel D

	Firing Temp (°C) and Time (min) for Test Pieces									
	1		2		3		4		5	
Slip Mix	Temp	Time	Temp	Time	Temp	Time	Temp	Time	Temp	Time
D1	870	6	880	8	850	10	860	10	850	12
D2	900	4	875	6	880	8	860	8	850	10
D3	880	3	840	15	860	8	855	12	845	10

Table A5: Firing Schedule for Enamel E

	Firing Temp (°C) and Time (min) for Test Pieces									
	1		2		3		4		5	
Slip Mix	Temp	Time	Temp	Time	Temp	Time	Temp	Time	Temp	Time
E1	860	8	855	8	850	8	845	8	840	8
E2	850	5	850	6	850	7	850	8	850	10
E3	840	10	880	4	900	4	870	5	800	5
E4	840	8	840	10	880	5	850	8	855	8

APPENDIX D

D. GLOSSARY OF ENAMELING TERMS

Adhesive Gums - Agar, arabic or tragacanth gums that bind powdered enamels to a surface and burn away in firing.

Backing Enamel. A mixture of odds and ends of 80-mesh enamels applied as a counterenamel to prevent warping.

Base Metal - The metal on which the enamel coating is applied.

Bisque - A coating of wet proceess enamel which has been dried but not fired.

Blistering - An enamel defect caused by presence of some contaminant foreign to good enamelling practice.

Burnishing - Smothening a metal surface with rounded highly polished hard metal tool.

Copperhead - Defect appearing as a small freckle pimple - like spot.

Counterenamel - Enamel fired on the back of a piece to equalize tension.

Crawling or Curling - A slumping effect caused by excessive enamel or gum application.

Crazing - Fine cracks

Dredging - Method of enamel application where the metal is heated to a temperature above the maturing temperature of the enamel before the coat is dusted onto the hot surface.

Emery Cloth: A cloth coated with fine grained abrasive material for smoothing and polishing metals.

Etching: Eating away of metal

Firescale: Metal surface residue resulting from exposure to high temperature in the kiln/furnace.

Firing Fork: A long handled two pronged tool for lifting trivets and firing racks into and out of the kiln.

Fishscale: Small, half-moon shaped fractures

Flux: A substance for promoting fusion.

Frit: Enamel in coarse particles

Gauge: A measurement to indicate thickness.

Groundcoat: A coat applied directly to the base metal.

Hairlines: Initial cracks which has been healed by fusion.

Inorganic: Not derived from vegetable or animal matter.

Kiln: A high temperature furnace for firing enamels.

Low Fire Enamel: Enamel that fuses at lower than 770^{o}C.

Mallet: A short-handled hammer with a large cylindrical head of wood, leather or rubber.

Metal Oxides: Colour ingredients in enamels derived from metals.

Mortar and Pestle: An extremely hard vessel and club-shaped implement for grinding enamels.

Oxidation: Discoloration of metal by exposure to heat, air or chemical.

Peeling: Detachment of pieces of enamel from metal

Pickling: Subjecting metal to an acid bath to soften and remove discoloration and soil.

Pinholes: A defect due to the fluidity of the groundcoat and the cleanness of the metal surface.

Pitting: A groundcoat defect due to contamination.

Planishing: Final light hammering to smooth out a metal surface.

Porcelain Enamel: A vitreous or glassy inorganic coating bonded to metal by fusion at a temperature above 440^{o}C.

Pyrometer: All instrument for measuring and indication temperature especially in a kiln.

Reboil: This defect occurs due to the evolution of gases from the base metal when it is heated to enamelling temperature.

Scribers: A pointed tool for scratching lines on metal star stilts - three or four pointed steel-tipped ceramic stilts for supporting pieces in the kiln.

Trivet: A pronged metal support for holding an enamel piece in the kiln.

APPENDIX E

E. CALCULATION OF OXIDE PERCENTAES IN FORMULATIONS

Table A6: Oxide Percentages in Fomula A

Material	m.wt	wt.%	K_2O	Na_2O	CaO	MgO	Fe_2O_3	B_2O_3	Al_2O_3	P_2OS	SiO_2	MnO_2	BaO	CoO	NiO
Feldspar	556	32	4.9		0.03		0.06		6.0		21.0				
Quartz	60	20									20.0				
Boric															
Acid	124	20						11.3							
Fluorspar	78	5			3.79										
Magnesite	84	2.5			0.09	1.05	0.01		0.02		0.1				
Whiting	100	5			4.74	0.04			0.02		0.06				
Barium															
Cabornate	197	5										3.88			
Soda Ash	106	4		2.34											
Sodanitre	85	3		0.82											
Cobalt															
Nitrate	291	0.5											0.13		
Manganese															
Dioxide	87	2.0										1.63			
Nickel															
Carbonate	119	1													0.6
Total			4.9	3.16	8.65	1.09	0.07	11.3	6.04		41.16	1.63	3.88	0.13	0.6
-Oxide			5.9	3.8	10.5	1.3	0.08	13.7	7.3		49.8	2.0	4.7	0.2	0.8

Table A7: Oxide Percentages in formula 8

Material	m.w	wt%	K_2O	Na_2O	CaO	NgO	Fe_2O	B_2O_3	Al_2O_3	MnO_2	SiO_2	TiO_2	CoO	NiO
Feldspar	556	30	4.6				0.06		5.7		19.6			
Quartz	60	30									**30.0**			
Boric														
Acid	124	15						8.5						
Salt														
Petre	101	6	2.8											
Magnesite	84	7.5			0.3	3.2	0.04		0.1		0.4			
Whiting	100	8			7.6	0.1	0.01		0.03		0.1			
Cobalt														
Nitrate	291	1										**0.3**		
Manganise														
Dioxide	87	1								**0.8**				
Nickel														
Carbonate	119	0.5												0.3
Salt	58	1		0.5										
Total			7.4	0.5	7.9	3.3	0.11	8.5	5.8	0.8	50.		0.3	0.3
-Oxide %			8.7	0.6	9.3	3.8	0.1	10	6.9	0.9	59.		0.4	0.4

Table A8: Oxide Percentages in Formula C

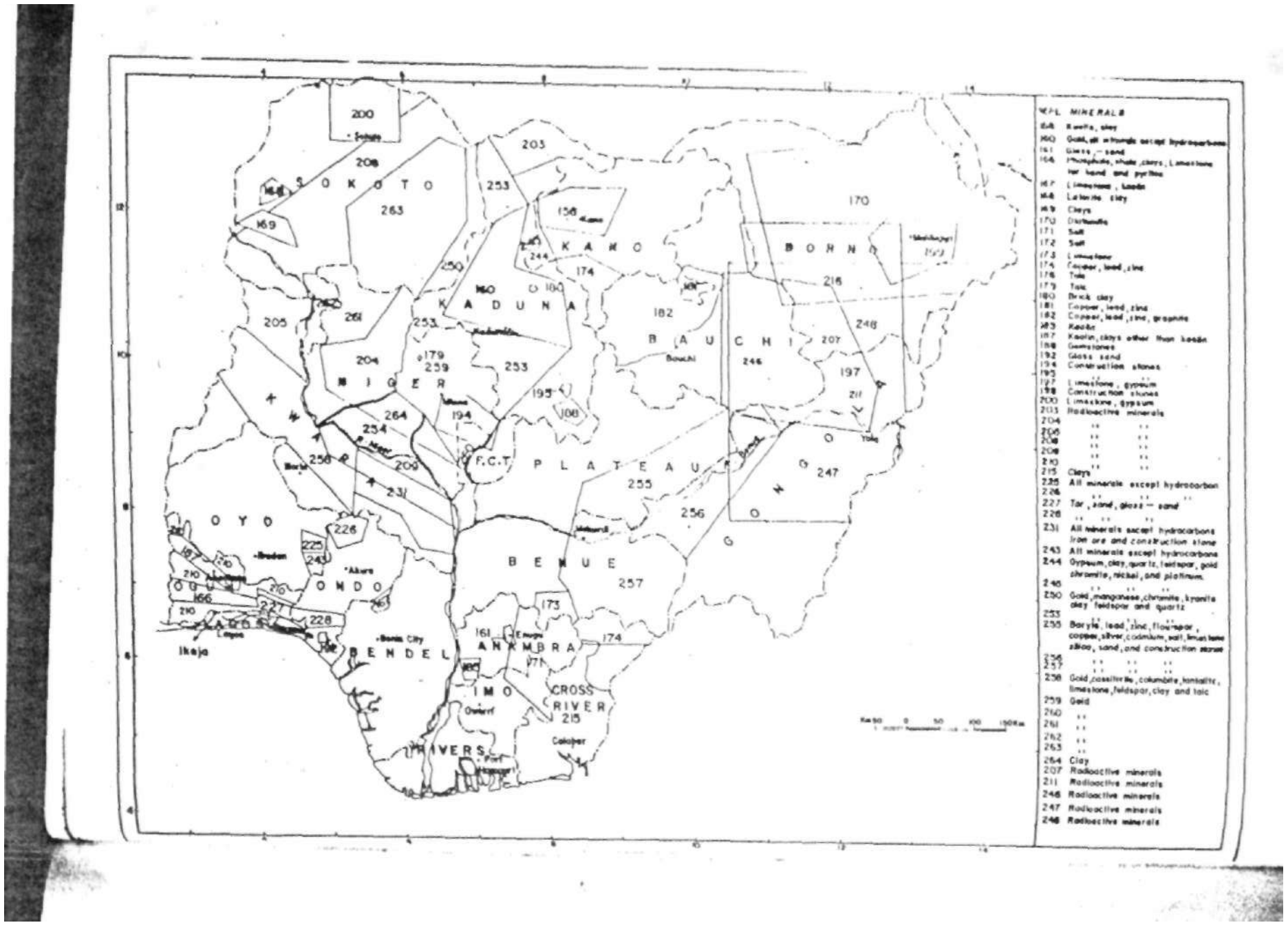
Material	m.w	wt.	K_2O	Na_2O	CaO	MgO	Fe_2O_3	B_2O_3	Al_2O_3	MnO_3	SiO_2	TiO_2	CoO
Feldspar	556	35	5.4		0.04		0.07		6.6		22.9		
Quartz	60	23									23		
Boric Acid	124	18						10.2					
Fluorspar	78	8			6.1								
Salt													
Petre	101	1.5	0.7										
Soda Ash	106	7		4.1									
Soda Niter	85	6		1.6									
Cobalt Nitrate	291	1											0.3
Manganese Dioxide	87	0.5								0.4			
Total			6.1	5.7	6.1		0.07	10.2	6.6	0.4	45.9		0.3
Oxide %			7.5	7	7.5		0.1	12.5	8.1	0.5	56		0.4

Table A9: Oxide Percentages in Formula D

Material	m.w	wt%	K_2O	Na_2O	CaO	MgO	Fe_2O	B_2O_3	Al_2O_3	MnO_2	SiO_2	CoO	NiO	BaO
Feldspar	556	25	3.8		0.03		0.05		4.7		16.4			
Quartz	60	25					0.1				24.9			
Clay	258	10	0.1	0.46	0.4	0.3	0.04		2.8		5.65			
Boric														
Acid	124	15						8.48						
Magnesite	84	6			0.2	2.5	0.03		0.06		0.28			
Whiting	100	4			3.8	0.03			0.0		0.0			
Soda Ash	106	3		1.76										
Soda														
Niter	85	2		0.54										
Manganese														
Dioxide	87	2.0								1.63				
Cobalt														
Nitrate	291	1.5										0.38		
Nickel														
Carbonate	119	0.5											0.32	
Salt	58	1		0.54										
Barium														
Carbonate	197	5												3.88
Total			3.8	3.3	4.4	2.5	0.22	8.48	7.6	1.63	47.	0.4	0.3	3.88
Oxide %			4.6	3.9	5.2	3.1	0.3	10.1	9.1	1.9	56.	0.5	0.4	4.6

Table A10 Oxide Percentages in Formula E

Material	m.w	wt%	K_2O	Na_2O	CaO	MgO	Fe_2O_3	B_2O_3	Al_2O_3	MnO_2	SiO_2	CoO	NiO
Feldspar	556	25	3.8		0.03		0.05		4.73		16.38		
Quartz	60	25					0.01				24.98		
Boric Acid	124	20						11.3					
Fluour-spar	78	8			6.1								
Whiting	100	1.5			1.4	0.01			0.01		0.02		
Soda Ash	106	8		4.68									
Soda Niter	85	6		1.63									
Cobalt Nitrate	291	1										0.26	
Manganese Dioxide	87	4.5							3.68				
Nickel Carbonate	119	1											0.6
Total			3.8	6.31	7.5	0.01	0.07	11.3	4.7	3.68	41.	0.3	0.6
Oxide %			4.8	7.9	9.4	0.01	0.1	14.2	5.9	4.6	51.	0.3	0.8


SOKOTO
KEBBI
KANO
BORNO
ZAMFARA
KADUNA
NIGER
BAUCHI
F.C.T
PLATEAU
OYO
OGUN
ONDO
BENUE
ANAMBRA
IMO
CROSS RIVER
RIVERS
BENDEL
Ikeja
Owerri
Calabar
Port Harcourt
Benin City
Akure
Ibadan
Lagos
Enugu
Makurdi
Jos
Yola
Maiduguri
Sokoto
Kaduna
Minna
Bauchi
Gusau
Abuja
Lokoja
Ilorin
Abeokuta
Oshogbo
Ado Ekiti
Awka
Umuahia
Uyo
Port Harcourt
Calabar
Owerri
Asaba
Benin City
Akure
Ibadan
Lagos
Enugu
Makurdi
Jos
Yola
Maiduguri
Sokoto
Kaduna
Minna
Bauchi
Gusau
Abuja
Lokoja
Ilorin
Abeokuta
Oshogbo
Ado Ekiti
Awka
Umuahia
Uyo
MINERALS
Kaolin, clay
Quartz, etc minerals except hydrocarbons
Gypsum, clay, quartz, feldspar, gold chromite, nickel, and platinum
Clays
Limestone
Coal, lead, zinc
Tale
Brick clay
Copper, lead, zinc
Copper, lead, zinc, graphite
Kaolin
Kaolin, clays other than kaolin
Gemstones
Glass sand
Construction stones
Limestone, gypsum
Radioactive minerals
Clays
All minerals except hydrocarbon
Tar, sand, glass — sand
All minerals except hydrocarbons iron ore and construction stone
All minerals except hydrocarbons
Gypsum, clay, quartz, feldspar, gold chromite, nickel, and platinum.
Gold, manganese, chromite, kyanite clay feldspar and quartz
Baryte, lead, zinc, flourspar, copper, silver, cadmium, salt, limestone silica, sand, and construction stone
Gold, cassiterite, columbite, tantalite, limestone, feldspar, clay and talc
Gold
Clay
Radioactive minerals
Radioactive minerals
Radioactive minerals
Radioactive minerals
Radioactive minerals