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US/SRL/78/207

SRI LANKA .

Technical Report: Development of glazes and colours*

Prepared for the Government of the
Democratic Socialist Republic of Sri Lanka
by the United Nations Industrial Development Organization

Based on the work of Ian Knizek,
Consultant in Glazes and Colours

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Summary of Recommendations

1. The formulation of the Piliyandala Transparent Frit as well as of all the color glazes manufactured with it should be revised and redesigned. (2.20)
2. Such redesigning will most likely take the form of substitution of the present transparent frit formula by another possibly a lead-bearing one of which examples have been offered in Annex I. Better glaze body fit and improved texture will be aimed at. (2.22)
3. The re-designing of the color glazes could, apart from frit substitution as per point (2), be accomplished through the introduction of new stains, examples of which are given in Annexes II and III. They allow to be used in much lower proportions thus contributing less to the viscosity of the molten glazes. (2.20)
4. More attention should be given to the frit-making operation. Its duration should be better controlled. (2.24)
5. Better controls of the particle-size distribution, slip density and all the rheological properties of the glaze-slips should be instituted. (2.24)
6. The frits shown in Annex I should be further improved, reproduced and tested under factory conditions. (2.22)
7. Since there are strong indications that the Piliyandala earthenware body exhibits a short densification range redesigning of its formula with the view of eliminating its Dolomite content is strongly urged. (2.30)

8. To avoid "spit-out" exclusively fresh bisquit for overglaze decoration (2.83) should be used.
9. Should this not always be possible the practice of slight opening of the backside of plates to facilitate faster elimination of the de-sorpted vapor should be intorduced. (2.83)
10. It is strongly recommended that the Ceramic Research Laboratory give assistance in the field of design, art-glaze development and supply to the handicraft centres operated by the Government's Small Industries Department. (3.00)
11. A Glaze & Color Section staffed by its own officer and suitably equipped (Annex IV) should be established as a part of the Ceramic Research Laboratory (4.00)

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Introduction

Within the framework of the UNIDO Project US/SRL/78/2207 Ceramic Research Laboratory, Piliyandala, Sri Lanka, Mr. Ian Knizek has been appointed Consultant in Glazes and Colors with the duration of three months. Attached to the Ceylon Ceramics Corporation he was to assist in the setting up of its central quality control and development laboratory and to advise on its effective use within the field of specialization. According to the Job Description US/SRL/78/207/11-56/32.1.B

- 1. Assess the present level of production technology, quality control and research in the field of glaze and color manufacture and application and identify areas of possible improvement in keeping with market requirements;
- 2. Scrutinize the currently applied glazes and frits and define the scope for gradually replacing imported materials (frits, oxide & ready-made glazes) by locally produced ones;
- 3. Demonstrate how the laboratory can contribute to the development, manufacture and testing of frits and glazes and initiate appropriate activities in this respect;
- 4. Develop a range of frits and glazes for the use of indigenous art potteries;
- 5. Define the need for additional equipment required by the laboratory to enhance its efficiency in this field;

2.

- 6. Prepare local staff to continue the work initiated through extensive on-the-job training.

Apart from endorsing the Consultant's **frame** of reference the Corporation's General Manager stressed the importance of periodic lectures to the Staff in the field of his specialization.

1.00 Summary of Activities**Immediately after arrival in field, the Consultant**

- 1) carried-out an investigation of the conditions under which earthenware (crookery) is manufactured in the Piliyandala Factory. The above investigation concentrated on the assesement of production losses due to defects of quality, proceeding later to the analysis of their causes.

No separate investigation has been made of the second earthenware factory of Negombo because the materials used there were the same as at Piliyandala. Furthermore, as this Consultant has been able to establish at the time of his previous visit to the Ceylon Ceramics Corporation's factories, manufacturing equipment and consequently the processes were much the same in both plants. This Consultant's findings and conclusions are Mutatis Mutandis applicable to either factory.

- 2) Taking advantage of the equipment at the Ceramic Research Laboratory, the Consultant then determined some of the parameters of the Body/Glaze complex. The aim here was to ascertain to which extent certain manufacturing defects could be traced to the characteristics of the Body/Glaze complex.
- 3) Following-up on the information obtained as per (2) the Consultant demonstrated the formulation and preparation of glazes differing in their composition and certain parameters from those presently employed at the C.C.C.
- 4) Still keeping to his frame of reference he also developed and demonstrated the preparation of certain glaze stains; the aims pursued here were two: (a) to ascertain whether and to what extent the appearance of the presently manufactured crookery could be improved

through the use of stains formulated on a somewhat different principles; and (b) to increase the range of color finishes that could be made available to the C.C.C.'s customer thus enhancing the sales appeal of the crockery.

- 5) In his lectures to the C.R.L.'s staff the Consultant demonstrated the principles involved in the development of glaze formulae. The example which was chosen was the development of a low-melting glaze formula for the use of handicraft potters. Here the Consultant demonstrated the effect of the ingredients and of their combination on such overimportant parameters as expansivity (which control glaze-body fit) and lead release in the case of lead-bearing glazes and water-solubility of lead-less ones. The use of both, the molecular and the percentual method was shown.

The Consultant also,

- 6) Travelled to Meepe to obtain from Lanka Refractories crucibles necessary for his work. Advantage was taken of their opportunity to visit the plant itself and assess for future references its potential;
- 7) To assist in bolstering Lanka Refractories sales efforts, the Consultant, invited by C.C.C.'s General Manager, visited in the company of his international colleagues the Cement Factory of Puttalam.
- 8) Towards the end of his mission he also visited several artisanal centres:
- a) a pottery shop operated by the Ceylon Ceramics Corporation at Ambalanmulla, Seecuwa;
 - b) Government Handcrafted Ceramic and Training Centre of Waragoda, Kelaniya, operated by the Department of Small Industries.
 - c) A similar but smaller Centre at Nittambuwa.

2.00 Glazes and Bodies at the Ceylon Ceramics Corporation

2.10 Present Glaze Formulations

Both the Piliyandala and Negombo factories use a transparent and an opaque glaze. For brevity's sake they will be from now on referred to as T or O respectively.

The molecular formulae calculated from batch recipes, as shown in Annex I reveal significant differences. Following normal procedures the 17% Zirconium Silicate smelted with other ingredients to produce frit O was disregarded in the calculation.

The most notable feature of either frit is the absence of lead; this is not quite usual for earthenware glazes maturing at Piliyandala gloss temperatures (about 1060° -1080°C). The proportion of alumina is just about right in frit O; in frit T alumina is about 0.13 equivalents too high; that circumstance may help to explain some of the characteristics of the glazes compounded with this particular frit.

These are colored glazes; green, blue-green, brown, pale-blue and yellow glazes have been used in the past. At the time of this Consultant's presence only the green and blue-green glazes were being produced.

2.20 Glaze Problems

The Consultant observed considerable pinholing specially in the green-colored glazes. This condition was, obviously accentuated when application thickness was too heavy. There was, also, considerable disparity in the glaze thickness most probably due to a combination of factors like the high viscosity of the molten glaze and heaviness of application thickness. The latter is undoubtedly caused by (a) variation of water absorption of the bisque and (b) lack of control of the glaze-slip consistency, viscosity and thixotrophy.

The fundamental cause of the observed pinholing is, of course the high viscosity of the glazes at the gloss-firing temperatures. This is the reason why all Piliyandala glazes show a tendency to pinholing.

Leadless, alkaline glazes are, generally speaking very viscous but the presence of Zircon in them does not help. That Zircon-opacified glazes tend to pinhole is a very well established fact. Nevertheless, it is possible to prepare pinhole-free finishes but only under best conditions of formulation and application.

One observation still has to be explained: the heavy pinholing occurring in colored glazes compounded with frit T which is Zircon-free. The answer is that a fair amount of Zircon is introduced even here in the preparation of the actual glaze. In compounding a typical colored glaze, 3 percent or more Zircon is added in addition to some 13 percent of the stain. This, in turn may contain as much as 20 percent of Zirconium Silicate (plus as much as 25 percent of silica & the same amount of feldspar; contrary to what is sometimes believed, feldspar introduced into glazes maturing at temperatures less than 1100°C does not act as a flux.) All these substances, i.e. Zircon, Silica and Feldspar are viscosity-enhancing.

Tests carried out in the Gradient Kiln confirmed the tendency of all Piliyandala glazes to pinhole when applied too thickly, i.e. over 0.020". Another fact revealed by gradient kiln was that the incidence of pinholes increased with increasing firing temperatures. This is not unexpected. Pinholes are nothing else but craters left in the glaze surface by exploding gas bubbles that rise to it. If viscosity is reduced, as happens when temperature is raised, more bubbles rise to the surface causing more pinholes. Under the condition of the gradient kiln less pinholes were observed at 1050°C than at 1030°C .

2.21 The Lead-Release Problem

The reason why such rather difficult glazes are preferred in the Piliyandala and Negombo factories is the fear of the poisonous nature of lead compounds. This Consultant would not want to minimize the health hazard involved in industrial uses of lead compounds. And still less does he want to change the way of thinking in this matter prevailing in the Ceylon Ceramics Corporation. He believes, however, that the matter must be discussed in the right perspective.

The fact is that the so-called 'Lead Scare' originated with some legitimate cases of lead poisoning ultimately traced to some indigenous pottery glazed with a mixture of red lead and little silica and fired at low temperatures. By the time the facts involved in these cases percolated to the general public the facts became distorted and their meaning considerably obscured. With the rise of environmentalist and conservationist movements the issue became emotion-laden.

The fact remains, however, that today many years after the events mentioned above very few earthenware manufactures use leadless glazes for gloss temperatures between 1000^o and 1100 C. That goes above all for the industries of the U.S. England, Germany, France and Italy.

It is now fully realized that lead-release as determined by means of the various testing methods (BS, ASTM, DINAFNOR) is a function of formulation. The fact that a lead-solubility (not lead-release as determined by the standardized test now in use) of a simple lead bisilicate could be decreased from the initial 4.59 percent to 0.7 percent by an addition of 0.254 equivalents of alumina, has been known since 1936.

More recently, and more significantly, work sponsored by the American Lead and Zinc Institute brought out facts that help much in formulating low-lead-release glazes:

- 1) A substitution of 0.1 molar equivalent of lead oxide by the equivalent of a combination of the three alkali oxides, Li_2O , Na_2O and K_2O has resulted in a 50 percent reduction of lead release of a cone 07 glaze based on a $\text{PbO} \cdot 1.3 \text{ SiO}_2$ silicate;
- 2) Similar results were obtained through the use of the combination of MgO , CaO and SrO but excluding BaO ;
- 3) Addition of Zircon in amounts not exceeding 0.1 equivalents reduced lead-release dramatically;
- 4) Repeated lead-release tests result in its decrease; in one case from the initial 0.1 PPM to 0.05 PPM. The meaning of this result is that lead-release of glazed pottery will decrease with use.
- 5) Lead-release decreases with decreasing glaze thickness.

2.22 Improved Glaze Formulations

The above principles have been applied in formulating a low temperature glaze for the use of handicraft potters. The starting composition is shown in Annex I under the number 14.

Due to the insistence on lead-free formulation a corresponding formula 13 has been worked out. At the time of drafting this report, the Consultant has not succeeded yet in producing and testing this frit. This, for lack of facilities (fritting kiln). It must be kept in mind that lead-free glazes maturing at 850° to 900°C are extremely difficult to formulate. Since they must be based on the use of alkaline oxides as bases, they tend to craze on bodies not high enough in silica. If alkali oxides are reduced and more boric acid added to compensate for the accruing loss of fusibility compositions of this type tend to become more water-soluble.

For use at Piliyandala and Negombo gloss-firing temperatures the molecular formulae of two lead-bearing frits 11 and 12 are given in Annex I. They have been in successful use for many years in several earthenware factories, giving consistently lead-release values under 5 PPM. Reproduced under Piliyandala condition frit 11 appeared a bit hard showing consequently some lack of gloss.

It is strongly suggested that a glaze of this general type be tested at Piliyandala. The final composition will stand somewhere between that of frit 11 and 12. Due to lack of time and facilities this Consultant was not able to make the adjustment himself. The arrived at composition should then be smelted in one of Piliyandala's rotary frit kilns, choosing for it a time immediately following its relining.

The Consultant believes that apart from giving a better pinhole-free finish it will permit better color development especially from chrome-calcium stannate stains. If proved satisfactory it could, with advantage, substitute the presently used glaze T especially in view of the fact that same does not fit well the Piliyandala body as will be discussed in a subsequent section.

2.23. Thermal Expansion and Glaze Fit

It is extremely difficult to evaluate glazes ignoring their thermal expansivity; glaze-fit and with it crazing resistance depend on it. These two are, of course, functions of the glaze/body complex. In other words the expansivity of the body has to be known as well. No determinations of thermal expansion could be made during the Consultant's work at the Laboratory. (The Mettsch Differential Dilatometer was out of commission and part of it has been shipped to Germany for repairs.)

An indication of the glaze/body fit can be obtained, however, through comparing moduli of rupture of unglazed and glazed bars. This the Consultant has done with both of the glazes

used in the Piliyandala factory. The obtained results showed that the bending strength of the bars glazed with the Q glaze exceeded that of the unglazed ones by a factor of 1.3 (635 kg/sq.cm against 434 kg/sq.cm). On the hand application of glaze T lowered the modulus of the bisque body by 3 percent (468 kg/sq.cm). The body covered with glaze Q is, therefore in compression while glaze T either induces a slight tension or is, expansion-wise, in equilibrium with the body.

These results are confirmed by the crazing resistance of the two glazes. Both, actual tests carried out by the Consultant himself and examination of the factory' own records indicated that under conditions of Piliyandala's autoclave test (one hour at 50 lbs. per sq. inch) the Q glaze does not craze even in five successive cycles. On the other hand objects covered with either glaze T or any of the colored ones compounded with frit T developed craze lines in the first exposure.

One hour at 50 lbs. per sq. inch does not represent very drastic conditions. Normally autoclaving should be carried out at 125 lbs. per sq. inch or the duration of the test extended to five hours. It may be concluded, therefore, that the glaze T does not fit the body it is used with.

As regards glaze Q , there is nothing wrong with it provided that its tendency to pinholing can be checked by stepped-up controls of viscosity, application thickness and grinding fineness. The glaze-fit is excellent; apparently enough of the silica of the added Zirconium Silicate remains in solution to impart the glaze a lower thermal expansion, this unproven assumption being reflected in the modulus of rupture figures quoted above.

2.24 Control of the Frit and Glaze-Making Operations

The importance of a close control of all the parameters involved in producing defective glaze finishes as discussed above can not be over-emphasized. Such controls will particularly include the following:-

- 1) Maintaining a uniform fritting temperature;
- 2) Uniformizing fritting time;
- 3) Closely controlling the grinding fineness through maintaining consistently uniform water/solids ratii and grinding times; checking particle-size distribution.
- 4) Maintaining uniform glaze-slip densities.

2.30 The Body

2.31 Moisture Expansion

The crazing results quoted above in 2.23. do not indicate only that the transparent glaze is unsuitable for the body it is used with. There is also more than a suspicion that its moisture expansion may be too high. Examination of the body formula showed that no special efforts were made to control this parameter through judicious additions.

The attempt was made to measure the moisture expansion of the factory-produce body. Result of the first autoclave exposure failed to confirm above suspicions; there was no moisture expansion; in earthenware bodies, an unheard-of phenomenon. Absorption determinations in the moisture expansion specimens showed it to be less than 1 percent which explains the odd results reported above.

2.32 The Use of Eutectic Fluxes in Earthenware Bodies

But still another conclusion could be drawn from these results. Namely that the body has a short vitrification range. This, if true, would be due to the 4.5 percent

dolomite used in the body. Eutectic fluxes like CaO and MgO are known to produce bodies with a short vitrification range. This circumstance probably explains the reportedly very wide variation in the absorption which are being observed. Elimination of the dolomite from the body formulation suggests itself.

2.33. "Spit-Out at Piliyandala

Information secured at the factory revealed that "spit-out" is endemic at the Piliyandala factory. Contrary to what is sometimes believed, "spit-out" is not a glaze problem; its a body problem. With earthenware, "spit-out" is nothing unusual. Unfortunately a sure-fire remedy has not been found yet. Since the phenomenon is caused by de-sorption of the humidity adsorbed by the glaze ware while in storage, "spit-out" can be avoided by using for over-glaze decoration exclusively fresh ware directly from the kiln and never one that has been stored for sometime.

It has also been found that assisting desorpted water vapour to escape prevents "spit-out". This is actually done by drilling small orifices into the back of the plates or by opening passages in the glaze coating by means of hitting it with a sharp-pointed steel tool.

In the effort to avoid, or anyway, reduce the incidence of "spit-out" one more factor has to be considered. Experience has shown that other factors being the same, both the degree and intensity of "spit-out" varies, somehow, inversely with water absorption, especially if same is under 10 percent. More exactly there is much less "spit-out" at absorptions over 10 percent, 12 percent being considered best.

This well substantiated phenomenon is being explained in terms of the assumption that at higher absorptions the pore system is more continuous making the body more permeable thus facilitating the ventilation of the de-sorpted humidity.

Another tentative conclusion but one to be seriously considered is that the shorter vitrification range of the Piliyandala body which favours extreme variations of water absorption is more likely to produce a higher proportion of less porous dishes more prone to "spit-out". This could easily be another argument in favour of eliminating the dolomite from the body formulation.

3.00 Glaze Stains

The formulations of various glaze stains was demonstrated. The tested formulae are shown in Annex II. As maybe appreciated the color range is confined to cobalt blues, greens and browns, for which materials were either available at the Piliyandala factory or could be acquired in Colombo. Stains of Annex II were tested in both glazes O & T. Additions generally varied from 1 to 5 percent. Most of the times 2 percent were sufficient. Pleasing hues were obtained. The proportions of stains that have to be added are, as may be seen, considerably lower than those of the stains presently in use. This has a double advantage. In the first place smaller proportions of stains increase the molten viscosity of the glaze much less. Secondly lesser stain volumes have to be processed.

Only one yellow stain No.36, the formulation of which did not require Zircon, could be tested. Yellow stains are these days based on the use of Zirconia with Vanadium and Praseodymium salts. Development of suitable composition of this type was not possible because the ordered Zirconium Oxide, indispensable for them has not arrived in time.

For the same reason no sky-blue stains could be tested; they, too, are based on the use of Zirconium Oxide and Vanadium salts. Selected formulae are, however given in Annex III. Traditional yellow stains are based on lead antimnate. Such compositions were not tested however, as they would unlikely develop well in lead-free Piliyandala glazes. It is suggested that formulae of Annex III be tested as soon as the required materials become available.

Development of pink-red stains was hampered because only extremely limited amounts of tin oxide were available. Nevertheless, two formulae are given in Annex II.

The Consultant recommends that those formulae which are found satisfactory be now reproduced on a larger scale and factory tested.

4.00. Handicraft Potteries

Ambalanmulla Seeduwa

This small pottery employing 16 people and using exclusively slip-casting is operated by the C.C.C. through its Negombo factory which supplies all its needs. It is surmised then that any input it may require would percolate to it from the Ceramic Research Laboratory through the Negombo factory.

Handicraft Centre of Waragoda

This unit supplies 16 small handicraft units all over the island with clay, glazes and colors. It's importance is therefore considerable. Judging by the aspect and the quality of the turned-out products this organization urgently needs assistance in the renovation and up-grading of its designs, as regards both forms and decoration.

Apart from this Centre together with all the other units should gain considerable advantage through the introduction of a new line of product based on the use of colored, textured and crystalline glazes. Such glazes are

generally unsuitable for mass production but on the other hand lend themselves eminently for handicraft production.

Such glazes could be developed at the C.R.L. and, since the amounts that would be ultimately used are unlikely to be large, they could be easily produced in the Glaze & Color Section, the establishment of which is argued in a another context. (5.00.)

5.00. Future of Glaze and Color Activities at the C.R.L.

Sooner or later and probably sooner the C.R.L. will have to extend its activities from the present testing i.e., fact-finding to actual ceramic products improvement and development. Only in this way will it be able through the employment of all of its resources to fulfill its potential in the service of the country.

Few fields of ceramics are more important than the manufacture of Glazes and Colors. Large amounts of these materials are still being imported and there is a particularly large and promising market among the manufacturers of wall and floor tiles. And there are of course other potential customers.

If it is desired that the C.R.L. enter this important field - and this expert believes it should; - then several things will have to be done. First of them is the appointment of an official to take charge of these activities. Since training by means of fellowship at commercial glaze manufacturers' plants is probably not feasible, placement in a ceramic research institute (ECRA comes to one's mind) will probably be the second best solution. Further up-grading could be accomplished

through the collaboration of UNIDO Experts and Consultants.

As important as the development of human resources is the procurement of facilities and equipment. Annex IV lists the minimum of facilities that will have to be provided.

6.00 Art Glaze Formulation

An addendum on Art Glazes, giving selected formulations is being prepared. Because of lack of time same is unlikely to be included with the present report.

Molecular Formulae of FritsT (Piliyandala)

0.349 Na₂O
0.056 K₂O
0.595 CaO

0.472 Al₂O₃ 0.567 B₂O₃ 2.557 SiO₂

O (Piliyandala)

0.168 Na O
0.128 K O
0.344 CaO
0.068 MgO
0.292 Ca)

0.312 Al₂O₃ 0.456 B₂O₃ 2.576 SiO₂

11

0.540 PbO
0.032 Na₂O
0.003 K₂O
0.425 CaO

0.437 Al₂O₃ 0.366 B₂O₃ 3.429 SiO₂

12

0.362 PbO
0.095 Na O
0.020 K O
0.523 CaO

0.234 Al₂O₃ 0.355 B₂O₃ 2.220 SiO₂

13

Na₂O 5.6%
K₂O 5.6%
ZnO 4.3%
SiO₂ 61.6%
Al₂O₃ 7.7%
B₂O₃ 15.3%

100.0

14

0.70 PbO
0.04 CaO
0.03 MgO
0.03 BaO
0.04 Na₂O
0.03 Li₂O
0.03 K₂O
0.10 ZnO

0.3 Al₂O₃ 0.35 B₂O₃ 2.5 SiO₂

ANNEX IIGlaze Stains Developed at the C.R.L.228

| | | |
|-----------------|-------|--|
| Chromic Oxide | 12.9% | Ball Mill wet, dry, calcine in Bisque Tunnel Kiln mill wet, wash by decantation, dry. |
| Zinc Oxide | 38.0% | |
| Tin Oxide | 4.4% | |
| Iron Oxide | 21.0% | |
| Aluminium Oxide | 23.1% | |

Grey-rose with glaze O

Medium brown with glaze T

2 - 5%

2629

| | | |
|---------------|-------|--|
| Chromic Oxide | 34.5% | Mix dry, calcine in Gloss Kiln, wet ball mill, wash by decantation, dry. |
| Ferric Oxide | 30.8% | |
| Zinc Oxide | 34.6% | |

Brown with glaze T, pink with glaze O

2%

3629

| | | |
|---------------|-------|--------------|
| Chromic Oxide | 34.5% | same as 2629 |
| Ferric Oxide | 15.4% | |
| Pyrolusite | 15.4% | |
| Zinc Oxide | 34.7% | |

Light Brown with T, Pink with glaze O

2 - 5%

214

| | | |
|-----------------------------------|-------|---|
| Cobalt Sulphate (Heptahydrate) | 35.8% | Dissolve in water, evaporate to dryness, calcine Bisque Kiln wet mill, wash & dry. |
| Ammonium Nitrate | 9.3% | |
| Aluminium Sulphate | 46.6% | |
| Chromium Oxide | 9.3% | |

Blue green with T & C

2%

ANNEX II (contd.)217

| | | |
|------------------------------------|-------|--------------------|
| Cobalt Sulphate (heptahydrate) | 63.3% | Mix dry calcine in |
| Potassium Dichromate | 36.7% | Bisque Kiln |

Dark green with T, light blue with O

2%

220

| | | |
|----------------------|-------|-------------------------------|
| Potassium Dichromate | 37.6% | Dissolve dichromate in |
| Silica | 20.8% | water & mix with remaining |
| Calcium Carbonate | 20.8% | ingredients, calcine in Gloss |
| Calcium Fluoride | 20.8% | Kiln, wet mill, wash & dry. |

Leaf-green with T, light gray-green with O

2 - 5%

36

| | | |
|--------------------|-------|-------------------------------|
| Stannic Oxide | 84.0% | Ball Mill wet |
| Silica | 13.5% | calcine in Sanitaryware Kiln, |
| Titanium Oxide | 1.5% | Ball Mill wet, |
| Vanadium Pentoxide | 1.0% | dry. |

52

| | | |
|----------------------|-------|--------------------------------|
| Aluminium Hydroxide | 48.0% | Dissolve dichromate in water |
| Zinc Oxide | 46.0% | & mix with the remaining |
| Potassium Dichromate | 6.0% | ingredients. Calcine at 1400°C |
| | | for 2 hours. |

CTP

| | | |
|----------------------|-------|---------------------------|
| Silica | 21.6% | Mix dry calcine at 1230°C |
| Calcium Carbonate | 31.0% | for 2 hours, mill dry |
| Stannic Oxide | 39.7% | Mix dry with |
| Potassium Dichromate | 2.1% | 3.9g Sodium Nitrate |
| Lead Acetate | 5.3% | 3.9g Calcium Carbonate |
| | | 3.9g Boric Acid |
| | | 0.9g Potassium Nitrate |

Calcine in Bisque Kiln; Mill
wet, wash, dry.

ANNEX II (contd.)PI

| | | |
|----------------------|-------|--------------------------------|
| Silica | 24.8% | Mix dry, add 1.6g Lead Acetate |
| Stannic Oxide | 41.6% | in solution and 1.9g Potassium |
| Calcium Carbonate | 31.8% | Nitrate; fire for 2 hours at |
| Potassium Dichromate | 1.8% | 1300 C; grind wet, wash & dry. |

ANNEX III

(Zirconia-Vanadium Stains)

(not yet tested)

Blue

| | | |
|--------------------|------|---------------------|
| Zirconium Oxide | 52% | Ball Mill wet, |
| Silica | 33% | calcine bisque kiln |
| Barium Carbonate | 8.5% | mill wet, dry. |
| Vanadium Pentoxide | 6.5% | |

Yellow

| | | |
|--------------------|-------|-------------------------|
| Zirconium Oxide | 87.0% | Ball Mill wet, |
| Titanium Oxide | 1.5% | calcine in Sanitaryware |
| Vanadium Pentoxide | 11.5% | Kiln, mill wet, dry. |

ANNEX IVEquipment and Facilities for the Glaze & Color Section

Space Required: approx. 40sq. meters

- 1 Digital Balance, 0.1g precision, 10 kg capacity (Sartorius or similar)
- 1 Balance, 50 kg capacity weighing range 0.4 - 50 kg, reading 10g.
- 1 Crucible Kiln, locally made 1)
- 2 High-pressure (7kg/sq.cm) atmosphere burners for LP gas 6 mm inlet.
- 2 Pressure regulators for the above 0-15 kg/sq.cm
- 2 Pressure gauges 0-15 kg/sq. cm.
- 1 Rotary Smelting Kiln, *) for charges up to 50 kg complete with LP gas burners and low-pressure air blower.
- 1 Complete ball mill assemble with 10 - 1 litre porcelian jars, complete with motor, speed reducer and a charge of balls.
- 1 Complete ball mill assembly with 6 - 4 litres porcelian jars, with ball charge, motor and speed reducer.
- 1 50 kg. (wet) capacity ball mill, complete with a charge of balls, electric motor and speed reducer.
- 1 Labor Filterpress 15 x 15 cm, 10 trays.
Pressure 7kg/sq.cm for operation with compressed air (Boulton).
- 2 Porcelain mortars and pestles 15 cm diameter.
- 2 Porcelain mortars and pestles 25 cm diameter.
- 1 Laboratory Dryer, approx. 1 cu.m., 30-200°C with ventilation.

ANNEX IV (contd.)

- 1 Trolley-mounted mobile high-vacuum pumping unit; suction efficiency, 150 litres/sec. Ultimate Pressure 1×10^{-6} mbar (Rudolf Brand GMBH & Co. W. Germany or similar)
 - 1 Model 1 Pascall Tripple Roll Mill, porcelain rolls.
 - 1 Pascall disc Grinder, 203 mm hardened steel grinding discs, 3 HP motor.
 - 1 Franz Ferro Filter, bench type, top-fed, for laboratory use.
 - 1 Air Compressor *)
- 120 Crucibles *)

1) An improved model is being presently tested at the C.R.L.

*) Full specifications will be given in an Addendum.