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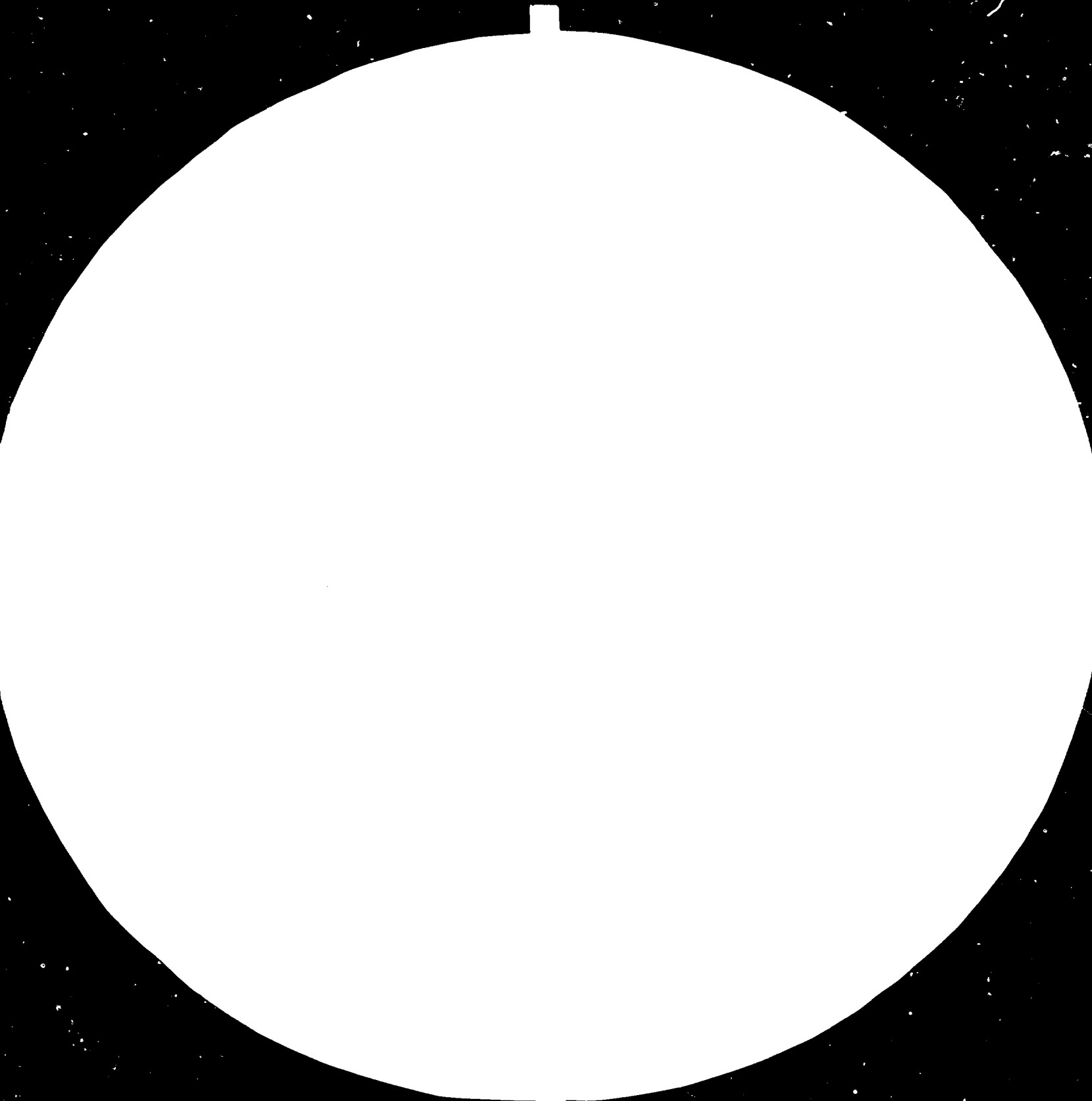
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MANUFACTURE OF LABORATORY PORCELAIN .

Basic Information *

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ABSTRACT

The paper deals with laboratory porcelain and its characteristic properties. The influence of individual body components as well as of some additional agents on its properties is described.

The importance of proper firing course and the most used technological ways of the production, casting and forming by plaster moulds are described, too. The description of liquefying process and examples of liquefying agents are presented together with the usability of single or double firing processes for various porcelain products.

TABLE OF CONTENTS

| | Page |
|--|------|
| ABSTRACT | 2 |
| I. INTRODUCTION | 4 |
| II. CHARACTERISTIC PROPERTIES OF LABORATORY PORCELAIN | 5 |
| III. PRODUCTION OF LABORATORY PORCELAIN | 12 |
| IV. FINAL NOTE | 17 |
| V. REFERENCES | 18 |

Figures:

| | | |
|---|---|----|
| 1 | Sphere of Laboratory Porcelain Body Composition | 19 |
| 2 | Influence of Firing Temperature on the Coefficient of Thermal Expansion | 19 |
| 3 | Liquefying Curve | 20 |

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I. INTRODUCTION

Laboratory porcelain is characteristic by its high thermal shock-, acid- and lye resistance and relatively high temperature of use. To reach successfully all these properties, it is necessary to follow the production technology from body preparation to firing process very carefully. With regard to these facts, it is recommendable to start the production of laboratory porcelain after a certain experience in the production of technical porcelain. The laboratory porcelain manufacture can be, therefore, successfully introduced in the developing countries with a certain tradition of porcelain production.

The increased requirements on the properties of laboratory porcelain and ways how to meet them are briefly described in this paper.

The UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries can extend all the technical assistance in establishing the production of laboratory porcelain in the developing countries.

II. CHARACTERISTIC PROPERTIES OF LABORATORY PORCELAIN

Some parameters of technical porcelain can be improved by applying a suitable body composition. The decisive requirement on laboratory porcelain is its good thermal shock resistance. Figure 1 shows the differences in body compositions of laboratory and technical porcelain.

Zapp ^{/1} compared body compositions and properties of numerous bodies for various purposes. He marked the sphere of bodies with good thermal shock resistance in the ternary diagram $\text{KNaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. After firing, it is the sphere limited by the following body composition:

| | | | |
|-------------------------|------|---|-------|
| KNaO | 1.0 | - | 4.0% |
| Al_2O_3 | 33.0 | - | 47.0% |
| SiO_2 | 59.0 | - | 66.0% |

The body compositions in question lie in the sphere of mullite deposition and their thermal shock resistance increases with the growing content of Al_2O_3 . A higher alumina content can be achieved either by increasing the kaolin content in the body or by substituting calcined kaolin, sillimanite or corundum for quartz. In spite of the moderately increased thermal expansion coefficient in the bodies with added corundum, the increased mechanical strength is a prevailing factor and good thermal shock resistance is preserved.

From the viewpoint of mineralogical body composition, it is necessary to minimize the content of free quartz in a fired body. Some producers do not, therefore, use quartz at all and the body is then composed of kaolin and feldspar only, the other use it very fine preground. Besides, such a type of siliceous material is used which has good solubility in a feldspar melt.

The next significant technical parameter of laboratory porcelain is its acid and lye resistance. It depends on the body composition proper and on the surface area. Mullite has the highest acid and lye resistance of all body components. Also vitrified feldspar, saturated with Al_2O_3 and SiO_2 , is well acid and lye resistant though not so well as mullite. Therefore, the laboratory porcelain with the highest Al_2O_3 content and minimum porosity shows the highest chemical resistance. In case of glazed products, chemical resistance of glaze is decisive. The glazed surface corrosion is caused by hydrolysis of silicates. The alkaline silicates incline to hydrolysis. They decompose for form alkaline hydroxides and a silicic acid gel ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$). This gel prevents the surface from further decomposition. Water diffuses slower to the surface through the thicker gel layer and thus further hydrolysis is slower, too. The corrosion rate of fused quartz is determined by the rate of surface layer hydrolysis and that of water diffusion through the protective coating of the silicic acid gel. The hydrolysis of bivalent metals (alkaline earths) and especially of aluminum silicates in comparison with alkaline silicates is much slower and the protective coating contains also soluble hydroxides beside the silicic gel.

The glaze solubility with the same molar content of metal oxides increases with the solubility of individual oxides. The solubility of oxides depends on their hydration heat according to which the oxides can be lined up as follows: K_2O , Na_2O , Li_2O , BaO , CaO , PbO , MgO , ZnO . This dependence is invalid to a certain extent for a vitreous body because the oxides affect one another there. If MgO is used instead of CaO up to 5%, chemical resistance is lowered, using a higher amount, it increases. Similarly, Al_2O_3 instead of SiO_2 in the amount of 2 to 5% has a negative influence on chemical resistance while the increase above 5% affects it positively. Also ZrO_2 shows a very favourable influence in chemical resistance.

Thermal shock resistance is determined by various factors:

- material constant defined by the coefficient of thermal expansion, modulus of elasticity, thermal conductivity and tensile strength
- concrete body shape; the decisive influence has the wall thickness and its homogeneity which affects the course of temperature gradients and thus the originating stress.

Beside these main factors, various stresses, evoked by the production technology used, have a considerable influence on thermal shock resistance, e.g. structural stress caused by various thermal expansion coefficients of individual porcelain body components, glaze stress, stress evoked during firing and annealing. Sandford and Liljegren ^{/4} examined the coherence between thermal shock resistance and physical properties (bulk density, coefficient of thermal expansion, heat conductivity, modulus of elasticity, bending strength, apparent porosity), and the content of vitreous phase and microscopic structure. They compared the measured values with the calculated ones from the given physical properties according to the formula of Winkelmann and Schott ^{/5}:

$$\Delta T = \frac{\sigma}{\alpha E} \sqrt{\frac{\lambda}{\rho \cdot c}}$$

where

- T = thermal shock resistance /°C/
- α = coefficient of thermal expansion /K⁻¹/
- E = Young's modulus of elasticity /Nm⁻²/
- σ = tensile strength /Nm⁻²/
- λ = heat conductivity /Wm⁻¹k⁻¹/
- c = specific heat /kJ kg⁻¹ k⁻¹/
- ρ = bulk density /kg m⁻³/

They found the only correlation between thermal shock resistance and coefficient of thermal expansion for the bodies with apparent porosity under 2%. Their thermal shock resistance increases with the decreasing coefficient of thermal expansion. No correlation between thermal shock resistance and the amount of the vitreous portion in the body was proved. They concluded that it is impossible to calculate thermal shock resistance from physical properties of bodies with sufficient reliability. Only the coefficient of thermal expansion can be considered. The higher the coefficient of thermal expansion, the higher the stresses at the same temperature gradient. This correlation, valid for homogenous bodies, is more complicated in case of porcelain with the heterogenous structure composed of several crystalline components and a vitreous component. There is no evidence that the thermal expansion coefficient of the body is the weighted mean of thermal expansion coefficients of individual components. However, the individual components influence the final coefficient indirectly - through the microstructure on which it is direct dependant.

Rado and Adgar ^{/6} remind the role of cristoballite in the bodies with the high content of clay components. Cristoballite can originate in the body either by transformation of amorphous SiO_2 or by transformation of crystalline quartz or by devitrification of vitreous phase which, with regard to its composition, belongs to the sphere of cristoballite deposition. In porcelain bodies with the high content of clay components, the two former sources prevail. Lundin ^{/7} claims that cristoballite creates either when the vitreous phase is saturated by SiO_2 or when the velocity of cristoballite creation is higher than that of dissolving SiO_2 in the vitreous phase. The coefficient of thermal expansion is comprehensively affected by cristoballite even if it is of small quantity or submicroscopically dispersed. The same can be stated in the case of prevailing mullite content.

These facts show the importance of the vitreous phase originating during firing. Its amount and viscosity depending on the body composition proper and firing conditions, influence quantitatively and qualitatively the phase body composition, its microstructure and final coefficient of thermal expansion. Consequently, the thermal expansion coefficient of the body can be affected by the content of fluxes, their choice and by firing conditions. The firing temperature influence on the coefficient of thermal expansion of porcelain of high clay amount and containing a varying alkali content is shown in Figure 2.

For the alkali content of 1.5%, the coefficient of thermal expansion is high even if the highest firing temperatures are applied; the amount of originating melt is insufficient within the given temperature limits of crystalline SiO_2 modification solution. The coefficient of thermal expansion is closely dependent on the firing temperature in case of the alkali content of 3%. The amount of the vitreous phase and its viscosity alternate in sympathy with the firing temperature and the crystalline SiO_2 modifications are completely soluted step by step. The alkali content having reached 4.5%, the amount of vitreous phase in the body is sufficient, within the given temperature limit, to solve the crystalline SiO_2 modifications. The thermal expansion coefficient is determined prevailingly by mullite phase.

Only the porcelain bodies of high alumina content achieved not by the higher content of clay components but directly by adding corundum, have very good thermal shock resistance even at the higher thermal expansion coefficient of the body. This increased thermal shock resistance brings about higher mechanical strength and better thermal conductivity of this body type.

Some authors claim that the course of firing, especially the phase of annealing, has greater affect on temperature shock resistance than the mullite content proper in the body. According to Hansson ^{/8}, the decisive factor is the rate of annealing in the temperature interval either of glaze transformation (in case of glazed products) or of vitreous phase transformation in the body (in case of non-glazed products). Therefore, the slowdown in annealing within the corresponding temperature interval of the vitreous phase transformation is recommended. Thus the stresses evoked in the body above this temperature can be eliminated by plastic flow.

The glaze influences thermal shock resistance of products in two directions: The glazed surface is smoother - it improves the mechanical properties of the body by lowering local stresses. More significant is the role of the stress between the glaze and body. It acts positively only in case of compressive stress. The stress intensity and its orientation depend principally on the ratio of thermal expansion coefficient of the body and the glaze applied as well as on the rate of annealing.

The next important technical parameter of laboratory porcelain is the maximum temperature of its use. The softening of the body at the growing temperature in consequence with the lowering viscosity of the vitreous phase obstruct the laboratory porcelain application at higher temperatures. However, the lowering of the vitreous phase viscosity is a necessary precondition of body sintering. Therefore, the maximum temperature of porcelain application must be lower than that of body sintering.

Bergdahl ^{/9} investigated in detail the process of softening and sintering in the system of kaolin - quartz - feldspar. The highest content of Al_2O_3 found in the bodies was 23%, i.e. the lowest limit for laboratory porcelain. The sintering temperature depends on chemical composition and decreases with the growing alkali content. On the contrary, it increases with the growing

Al_2O_3 content to the detriment of SiO_2 at the constant alkali content. With the growing alkali content, the temperature at which the deformation of fired bodies begins decreases more rapidly than the sintering temperature. On the contrary, with the growing Al_2O_3 content, it increases more quickly than the sintering temperature. The higher temperature of the laboratory porcelain use can be reached by increasing either the alumina content to the detriment of SiO_2 or the alkaline earth content in fluxes to the detriment of alkalis. Nevertheless, the latter possibility increases simultaneously the sensitivity of products to deformation during firing.

The glaze behaviour in glcw, i.e. its fusibility and fluidity or the temperature dependence of its viscosity, represents another important factor. The glaze viscosity is an exponential function of temperature. Na_2O decreases it more significantly than K_2O and a small amount of MgO substituting for CaO acts in the same way. The substitution of SiO_2 for Al_2O_3 increases the glaze viscosity every time. The addition of B_2O_3 and MgO is favourable to reach the higher temperature of glaze softening.

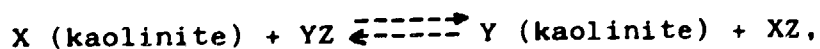
The rising Al_2O_3 content, especially in the form of mullite, influences the thermal shock resistance and maximum temperature of the laboratory porcelain use positively. Schroeder^{/10} informs that he reached up to 70% of mullite in the body composed of 35% of kyanite, 33% of potassium feldspar, 17% of kaolin and 15% of clay marked "Ball Clay". The mullite used was of a very fine crystalline form. Schroeder added ZrSiO_3 or TiO_2 to obstruct growing the crystals. The bodies of such composition proved very good mechanical properties.

III. PRODUCTION OF LABORATORY PORCELAIN

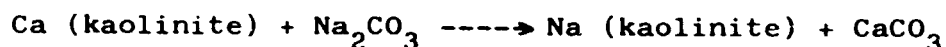
The most used technological way of the laboratory porcelain production is casting and forming by plaster moulds. The porous plaster mould makes the ceramic slip dewater and a compact ceramic body creates on the inside walls of the mould. Correct casting slip must comply with the following requirements:

- to have low viscosity and flux limit to fill the plaster mould having the content of water as low as possible
- to have the lowest possible propensity to settle the coarser particles and to change viscosity
- to have the capacity of creating a homogenous cast body of sufficient stiffness.

The process of minimizing water content in ceramic suspensions is based on their liquefying, i.e. reducing viscosity and flux limit. The process is a very sophisticated colloidal-chemical process which has not yet been explained satisfactorily. All hypotheses are based on the fact that the particles of clay minerals (kaolins and clays) have the capacity of binding ions to their surface. The bulk quantity of the adsorbed ions depends on the granularity, mineralogical composition and crystallographic structure and each mineral has it comparatively constant. This quantity is called the sorption capacity and it is expressed by miliequivalents per 100 g of dried matter. The adsorbed ions are bound to the surface of kaolin comparatively loosely and their substitution for other ions runs easily provided the latter are present in sufficient quantity in the solution which surrounds the particles of kaolin or clay. The exchange reactions are of equilibrium character and run according to the model:



where YZ and XZ are salts which have x^+ cation or y^+ cation and anion z^- in the solution surrounding the particles of kaolin. In case that the from-kaolin-liberated ions are removed from the solution in the form of an insoluble composition, it is possible to do this exchange quantitatively:



The viscosity of the ceramic suspensions is affected to a great extent by the kind of ions. From the point of view of the coagulating or dispersing power, ions can be arranged:

great coagulating power --- H --- Al---Ba --- Si --- Ca ---
--- Mg --- NH₄ --- K --- Na --- Li --- best dispersed ones

The grade of binding power of ions to the surface of particles goes up from right to left in this sequeention.

Apart from the appropriate liquefying agents the indispensable condition of the liquefying of ceramic suspensions is the presence of organic matters of colloidal character which most of kaolins and clays contain per se. These high-molecular organic matters (protecting colloids) create an envelope of particles which is the means preventing their coagulation.

The usual liquefying agents applied in industrial practice most are water and soluble glass, among the most efficient ones sodium, phosphates, especially hexameta phosphate can be listed which coagulate Ca and Mg ions and reduce the apparent viscosity. Humic acids, carboxy methylcellulose, oxylignu sulphonates in the form of soda salts are protecting colloids.

The necessary quantity of electrolyte and relation between the apparent viscosity of ceramic suspesnsion and the concentration of liquefying agents can be determined by means of the liquefying curve (Figure 3).

While the concentration of electrolyte goes up, the apparent viscosity goes down rapidly until it amounts to the minimum. Then, the enhanced concentration of electrolyte makes the viscosity go up slowly and when the solution is over-saturated the coagulation of the suspension sets in. The important factor which must be taken

into consideration in the manufacture is the stability of ceramic suspension which can be set out by the alteration of the apparent viscosity during storing. Consequently, the optimum liquefying is determined not only by setting out the apparent viscosity immediately after having stirred the suspension but after a certain period of time.

There are not only ions bound to the surface of clay particles but additional ones added by diluting water with the exception of distilled water. While former works knew the unfavourable effects of cations only, Mg and Ca especially, the new researches of German authors ^{/11} draw attention also to the unfavourable effects of some anions. Namely, anions Cl^- and NO_3^- were proved to increase the apparent viscosity of ceramic slips. Above all, the industrial water shows considerable swings in content of cations and anions and, therefore, if it is impossible to treat the water, drinking water will serve better.

The stiffening of the ceramic body which touches the plaster mould, runs very quickly first, then the velocity is reduced by the time. The time "t" necessary to create the stiff body chick "S" can be derived from the equation:

$$t = k_1 S^2 \quad \text{where } k_1 \text{ varies from } 1.0 \text{ to } 1.3 \text{ mm min.}^{-0.5}$$

From the parabolic course necessitates that the velocity of the process is controlled by the diffusion, first in the direction to plaster mould and after reaching a certain thickness of the stiffened body, the water is drained off by the created ceramic body.

The technique applied to the production of laboratory porcelain is plaster casting. The suspension is poured in the clasped plaster mould (it is recommended to revolve the mould during pouring), the suspension is left in the mould until the body reaches desirable thickness and then the residue is siphoned. Hollow cast body will

dry up after a certain period of halting and the resulting small shrinkage makes it separate from the mould walls.

The casting technique does not guarantee the uniform thickness of the product which is one of the properties bringing about the favourable resistance against the sudden temperature changes. Consequently, the products subdued to the temperature changes (melting crucibles) are additionally jiggered. Casting slip is prepared in two ways:

- direct grinding of raw materials with added electrolyte in drums

First, non-plastic raw materials are milled together with a small quantity of kaolin and necessary water, then electrolyte and the rest of plastic raw materials are added.

- wet grinding, filter-pressing and preparation of filter-pressed cakes in the blunger together with electrolyte

One-day maturing of the suspension is recommended to make all the reactions run before casting. Providing the rejects from casting are applied, the humidity and electrolyte content must be controlled additionally.

The determination of bulk density and apparent viscosity is sufficient to check the quality of ceramic suspensions for casting providing the raw material input, granularity of ground materials and quantity of electrolyte are kept within the technological recipe. The apparent viscosity is determined by the rate of flow of the suspension under constant temperature since the viscosity goes down at enhanced temperature.

The high content of clay raw materials which assures good heat resistance of the laboratory porcelain is not suitable to casting. Consequently, it is recommended that the content

of kaolin or kaolinitic clays in the body be kept within 40 - 45%. The rest should be calcinated material. This principle has an additional desirable effect, the shrinkage of the body is lower. The applied kaolins or clays must be of appropriate casting properties or they must be treated by the protecting colloid additives. Concurrently, they must have sufficient strength in green state.

Thick-wall glazed products can be manufactured by single firing process to reach the required sintering temperature. Those with thin walls (melting crucibles and evaporating pots) must be subdued to the double firing process. First biscuit is fired, then after glazing the glost firing sets in.

IV. FINAL NOTE

Following the request of Messrs. Industrial Ceramics, Hyderabad, India, to the UNIDO Headquarters - Vienna, the UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries in Pilsen completed this publication to assist producers in developing countries intending to expand their production of technical porcelain in this field.

The UNIDO-Czechoslovakia Joint Programme is ready to contribute to the establishment and development of laboratory porcelain manufacture in developing countries by research and advisory activities, training of technicians from developing countries in Czechoslovakian production plants, by raw material testing and by organization of twinning arrangements between the respective institutions in developing countries and the appropriate ones in Czechoslovakia.

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Figure 1: Sphere of Laboratory Porcelain Body Composition

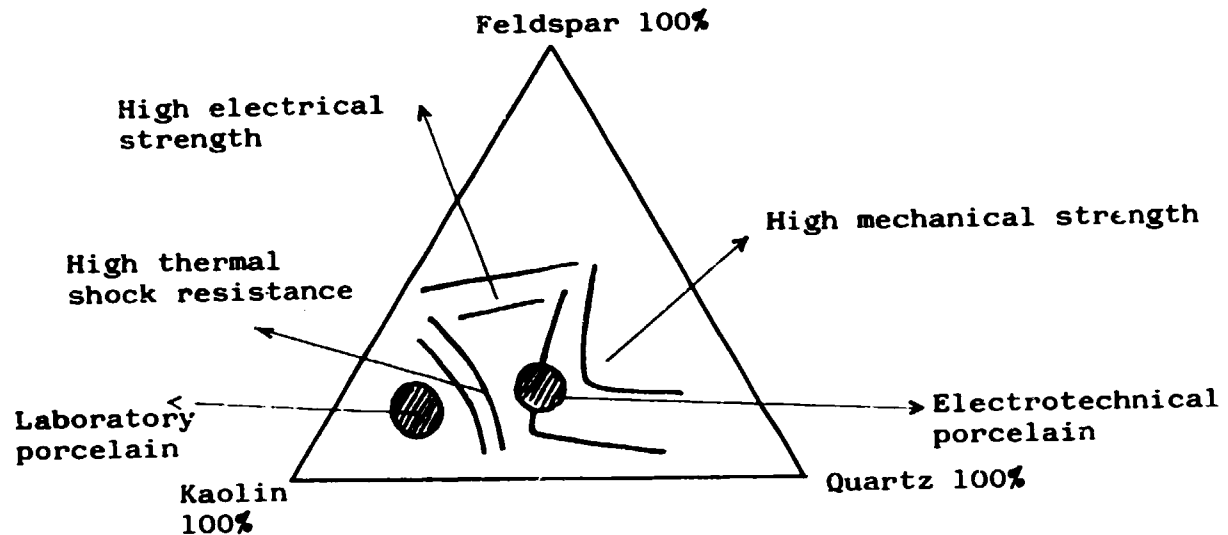
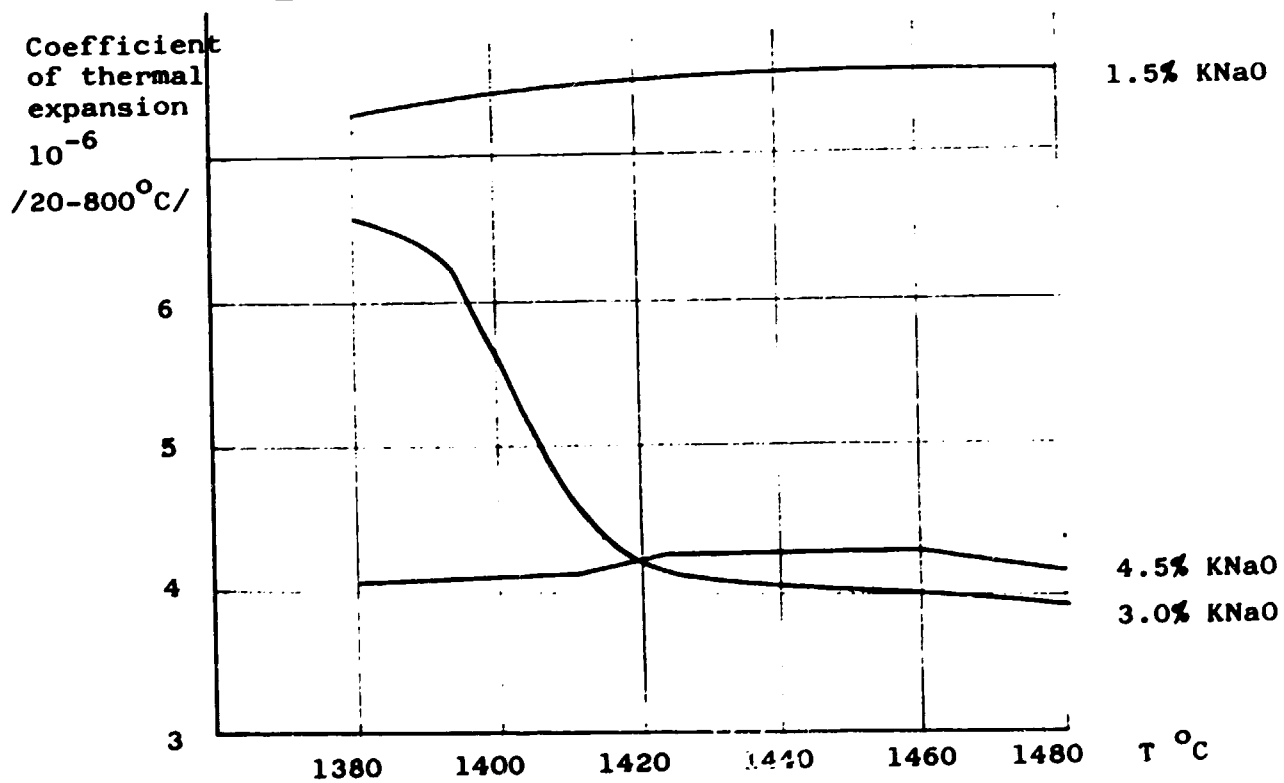


Figure 2: Influence of Firing Temperature on The Coefficient of Thermal Expansion



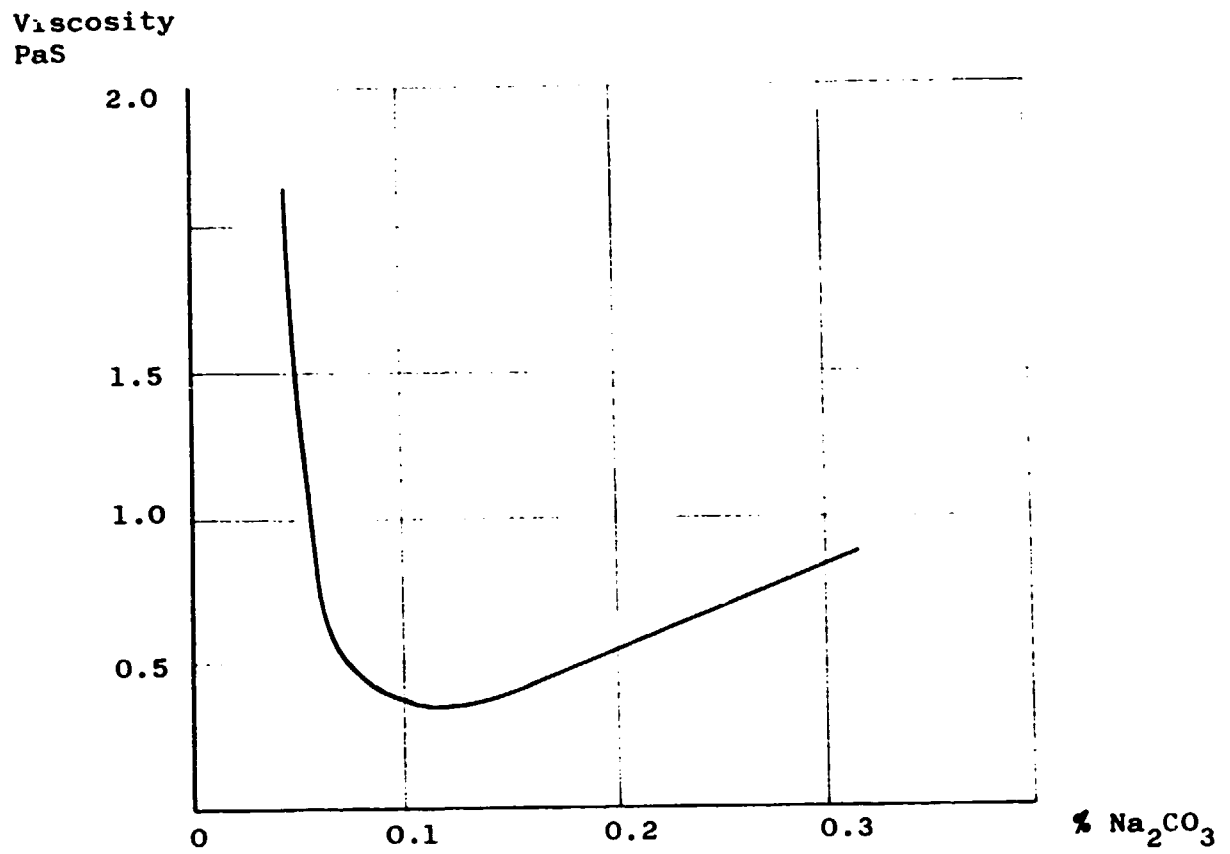


Figure 3: Liquefying Curve

