OBTAINING OF BISCUIT BODY FOR WALL TILES ON KAOLIN SAND BASES

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ABSTRACT

The present issue deals with the recipe composition of white biscuit bases for porous wall tiles. In this study plastic clay, low-plastic clay, kaolin, dolomite, limestone and kaolin sand are used as raw materials.

The interesting fact here is, that this type of kaolin sand resists industrial enrichment in the well known conventional methods because of micronizing and amorphizing of the clay minerals. The values of the physico-mechanical characteristics of the clay substance extracted from the kaolin are with 20-30% higher than these of the same products from the neighbouring deposits. These peculiarities are necessary prerequisites for creating a technology-recipe compositions for production of porous wall tiles and at the same time an easily approachable and perspective natural raw material is utilized.

In the study the physico-mechanical and thermal characteristics of wall tiles are defined. Data of chemical analysis and diffractograms of X-ray analysis are also presented. The mechanism of the phase formation of the ceramic body is explained, according to the starting composition. Three crystal phases are determined - quartz, anorthite and wollastonite.

The influence of the basic technological parameters on the production of wall tiles is studied.

The results are used for the introduction of an optimal composition under industrial conditions. At present 15.000 sq. m of wall tiles with porous body are being produced everyday with the above-mentioned recipe.

INTRODUCTION

The porous wall tiles with white and red body find wide application in the field of industrial and housing construction. They have a number of advantages, such as good strength, chemical stability, crazing resistance and give an opportunity for various decorations on the glaze. Their production is known from hoary antiquity and at present is topical of the day all over the world. The manufacture of structural clay ceramic products has gained a great experience and has given the preconditions for transition from manual production to industrial organization, characterized as high-level automated and providing a good control at every stage of technology. The main advantage is, that raw materials are accessible and widespread (1,2). Nowadays new sources for raw materials are being used in production of wall tiles (3,4). These are waste products from different branches of industry: metallurgy, machine-building, chemistry, light industry. A wide variety of raw materials is being used as well. In the USA and the USSR the tendency is for manufacture of white firing tiles, based on pyrophyllite and wollastonite (5,6). More and more often in the composition of clay ceramic bases mixed type raw materials are being introduced, which contain several components: silica sand, feldspar and clay substances (7).

The aim of the present work is to investigate the possibility for utilization of a natural raw material - kaolin sand in the production of white wall tiles. To study the main physical and chemical changes in the biscuit base, during the heating with view to improving the properties of firing biscuit bodies, designed for industrial construction.

EXPERIMENT

The compositions of the investigated ceramic bases are represented in Table 1. Their formation is based on the results of base-0, which was checked in industrial conditions. In the new compositions, silica sand and a part of kaolin are substituted for kaolin sand varying in terms 22-34%.

Table 1 Compositions of clay ceramic bases

COMPOSITIONS RAW MATERIALS	0	1	2	3	4	5	6	7	8
kaolin	29	20	20	21	18	18	20	20	18
kaolin sand	-	22	24	26	28	30	32	33	34
clay A	10	9	9	10	10	10	12	12	13
clay B	8	12	10	8	8	8	6	6	7
dolomite	11	10	11	11	8	8	16	15	-
limestone	9	12	10	9	12	14	7	7	28
feldspar	3	3	4	5	4	-	-	-	-
glazed body	-	-	-	-	-	-	3	-	-
biscuit body	12	12	12	10	10	10	4	7	14
bentonite	-	-	-	-	2	2	-	-	-
silica sand	18	-	-	-	-	-	-	-	-

The kaolin sands are raw material for preparation of enriched kaolin. They are situated in big Karst deposit bags with irregular form, at different depth. The content of silica sand and enriched kaolin is respectively around 75-80% and 20-25%. The chemical composition is shown in Table 2. There are some deposits in which the clay substance consists of particles under 1 m in size (more than 90%) and its mineral composition shows a tendency to amorphization, followed by increasing of kaolinite content in sands. This kind of kaolin sands is not processed by hydrocyclone enrichment method, because this would lead to great problems in industrial production-kaolin fraction does not precipitate and it is impossible to filterpress. The kaolin sand with higher kaolinite content has increased plasticity (32) and bending strength (1.6-1.8MPa) in comparison with adjacent deposits, which is a precondition for its utilization in wall tiles production.

Table 2 **Chemical composition of raw materials**

OXIDES RAW MATERIALS	Loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O
kaolin	11,91	50,88	33,78	0,91	0,37	0,27	0,75	0,49	0,64
kaolin sand	2,99	86,74	8,30	0,33	0,20	0,53	0,59	0,11	0,21
silica sand	0,40	98,90	0,30	0,10	-	0,30	-	-	-
clay A	9,14	55,28	26,48	1,42	1,48	1,72	0,83	1,37	2,28
clay B	8,47	62,27	20,84	2,96	0,98	0,56	1,60	0,96	1,36
bentonite	6,61	71,69	11,89	2,35	0,10	4,56	1,09	0,33	1,38
feldspar	0,48	73,30	16,61	0,10	0,03	0,57	0,18	8,39	0,34
limestone	43,95	0,08	0,13	-	-	55,39	0,45	-	-
dolomite	45,25	1,85	0,34	0,14	-	32,02	20,40	-	-

Two more clays A and B, and enriched kaolin are introduced in clay ceramic bases with chemical composition given in Table 2. Clay A is specified as a hydromica-kaolinite type, dark grey in colour with ingredients of quartz, feldspar, muscovite and a large quantity of fine carbonized particles with vegetal origin. Clay B is kaolinite type with lower Al_2O_3 content, its colour varies from light to dark grey. The enriched kaolin obtained from kaolin sand possesses high whiteness and contains mainly kaolinite, hydromica, muscovite with quartz impurities, feldspar, carbonate, zircon, garnet, limonite and others. Small quantities of feldspar, bentonite and biscuit base take part in the compositions of bases in order to improve physical and mechanical characteristics of wall tiles. Alkali-earth raw materials content is in terms 20-23%.

RESULTS AND DISCUSSION

Ceramic wall tiles are characterized with respect to their properties (Table 3): strength in green and dry state, strength after biscuit firing, strength after glaze firing, shrinkage, water absorption and thermal stability.

Table 3 **Characteristics**

COMPOSITIONS CHARACTERISTICS	0	1	2	3	4	5	6	7	8
R-in green state,MPa	0,57	0,61	0,54	0,60	0,59	0,58	0,57	0,58	0,54
R-after drying, MPa	1,91	2,31	2,19	2,45	2,33	2,23	2,01	2,27	2,09
R-after biscuit firing, MPa	13,2	14,6	13,5	16,7	13,8	14,1	14,9	15,5	16,0
R-after glaze firing, MPa	15,6	17,2	16,1	21,0	16,6	17,2	18,5	19,2	20,3
water absorption, %	24,9	22,8	22,6	22,7	23,6	23,1	23,1	23,4	24,9
shrinkage, %	0,25	0,20	0,20	0,15	0,10	0,15	0,15	0,15	0,03
thermal stability,ºC	150	160	160	160	160	160	170	170	180

The kaolin sand contains up to 25% kaolinite, which relates it to the lean materials group. Because of this, kaolin sand does not influence the properties of wall tiles in green state. Small amounts of bentonite added to clay ceramic bases do not change the strength of wall tiles in dry state. It can be explained with the fact, that the bentonite used must be chemically activated in advance, in order to gain high binding power.

It was found out, that after the firing of experimental biscuit bases the compositions with higher kaolin sand content, possess higher bending strength. The same relation is observed in the data of the strength for glazed wall tiles. The shrinkage is maintained favourably in normal terms (0,03-0,25%):

Its positive influence on physical and mechanical characteristics probably is due to the formation of a larger quantity of crystalline phases, which build the biscuit bases. This conjecture is of interest to be clarified. The deformation on straight line, angle and diagonal line is measured for all compositions. Only composition 8 showed a tendency to torsional strain on diagonal. The deformation of wall tiles depends on phase transitions during the heating and on their thermal expansion. For this reason compositions 1,8 are investigated by means of thermal analysis (Fig. 1A, B).

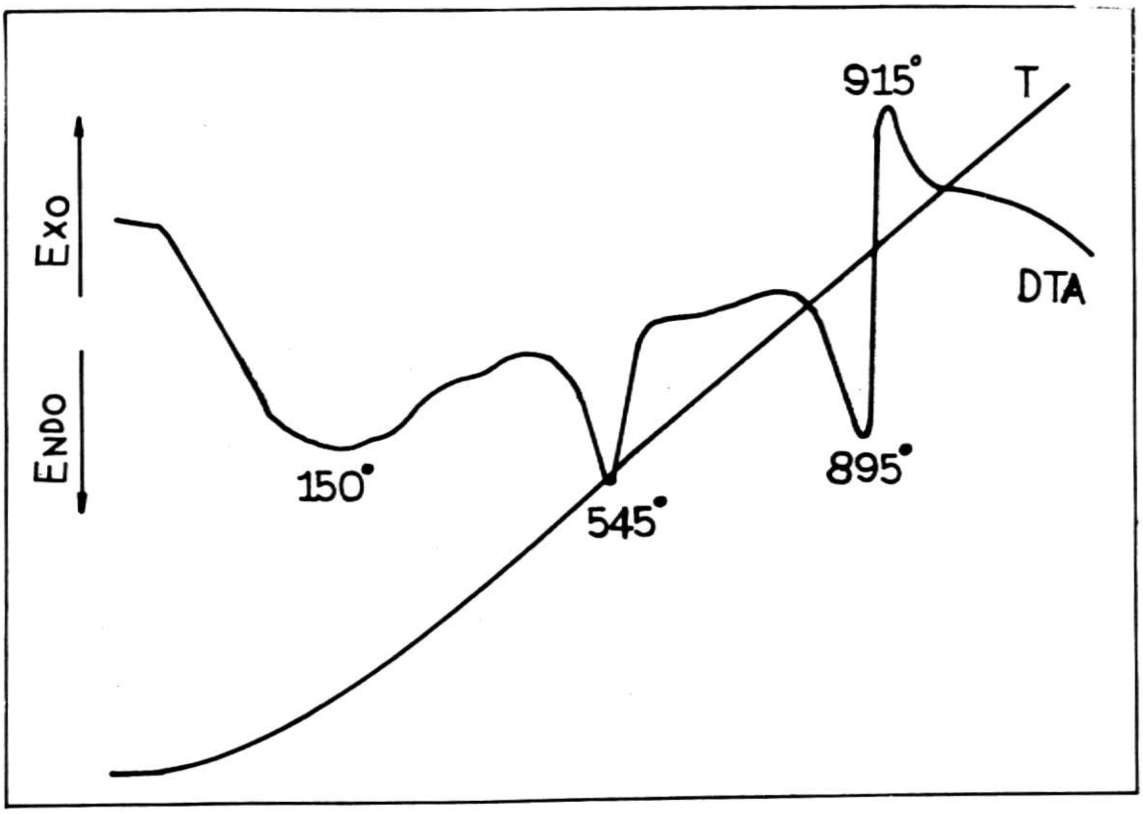

Fig.1A: A DTA trace of composition 8

On DTA trace of recipe 8, three endothermal peaks can be seen. First at 120-180ºC, which can be attributed to the evaporation of absorbed water, second at about 545ºC - in consequence of chemically bonded water in plastic components. The third endothermic peak at 895-915ºC is due to $CaCO_3$ dissociation. The presence of dolomite in the composition of bases changes the form of DTA trace (Fig. 1, B) and for recipe 1, two more endothermal peaks can be seen at about 780ºC and 845ºC due to dolomite decomposition.

The linear variations which occur at the formation of ceramic body are represented at Fig. 2. At temperatures up to 600ºC a rectilinear expansion of the samples is observed, at higher temperatures intensive shrinkage occurs, which is related to the destruction of clay minerals crystal units. It may be seen, that the shrinkage slope of the compositions with dolomite is wider than the slope of recipe 8, which is sharper and with larger area. The maximum values for linear variation of the samples, depend on the silica content and the kind of carbonates. The greatest shrinkage is observed in temperature range 850-960ºC. According to DTA and XRD results, at these temperatures the final decomposition of carbonates occurs and the phase formation of galenite, anorthite and wollastonite. At temperatures above 960ºC the second stage of expansion begins, which compensates for the lump

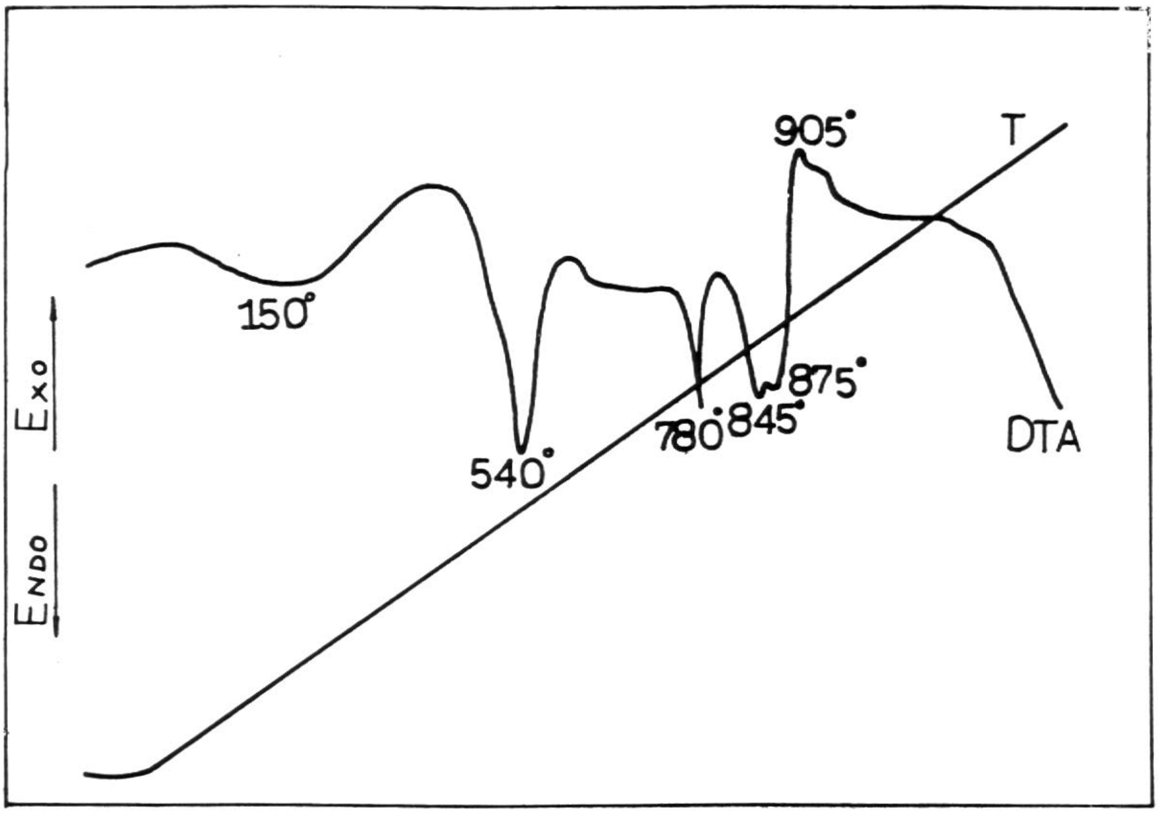

Fig.1B: A DTA trace of the composition 1

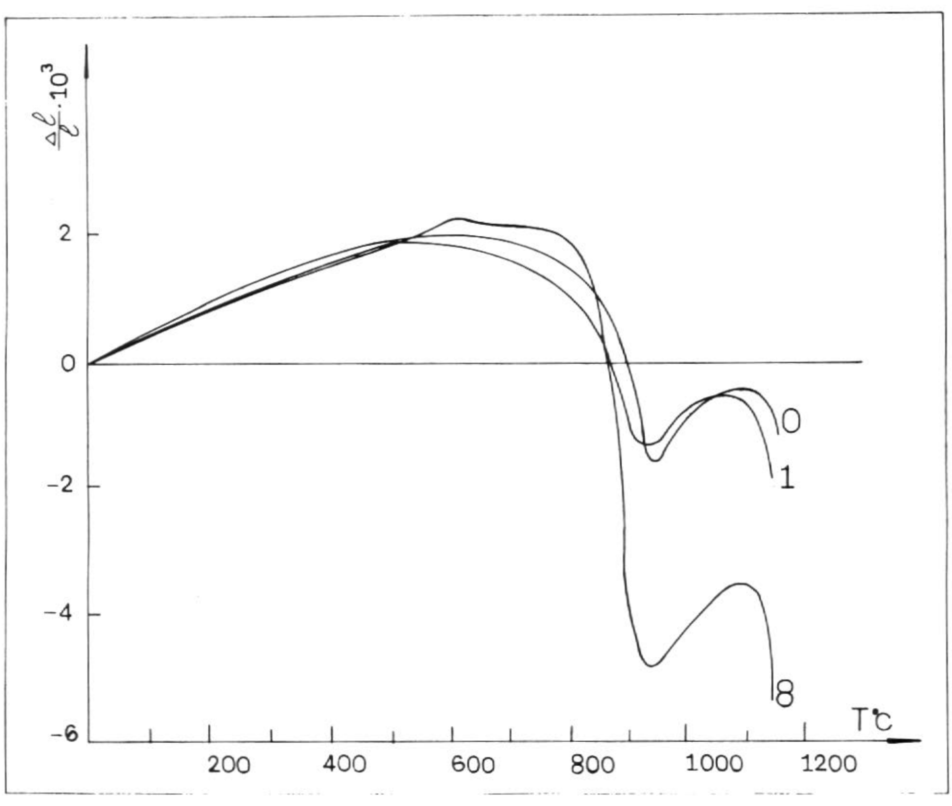

Fig. 2: Thermal expansion of clay ceramic bases; compositions 0, 1, and 8

shrinkage. It must be pointed out, that the secondary expansion extremely depends on CaO content and on the kind of raw materials, which CaO is introduced by. The shrinkage ratio in temperature range 850-960ºC and the following secondary expansion are in direct dependence on wall tiles deformation, which is proved by investigations. The experimental wall tiles made from composition 8 (28% CaO) underwent considerable torsional strain on diagonal line ±1,36 mm. The maximum value for the expansion of the investigated samples is observed in temperature range 1020-1120ºC and at higher temperatures a final shrinkage starts.

By means of X-ray diffraction three crystal phases are identified, quartz, anorthite and wollastonite in the specimens of biscuit wall tiles, firing at 1080ºC (Fig. 3). The diffractional peaks of wollastonite for recipe 8 are greater than the peaks for recipe 1, which is an evidence for higher wollastonite content. With the presence of this phase the improved mechanical strength of biscuit bases after firing, obtained with participation of kaolin sand can be explained. It must be mentioned that wollastonite phase is attended by undesired deformation. The phase composition of the other investigated biscuit bases is similar to the phase composition of recipe 1.

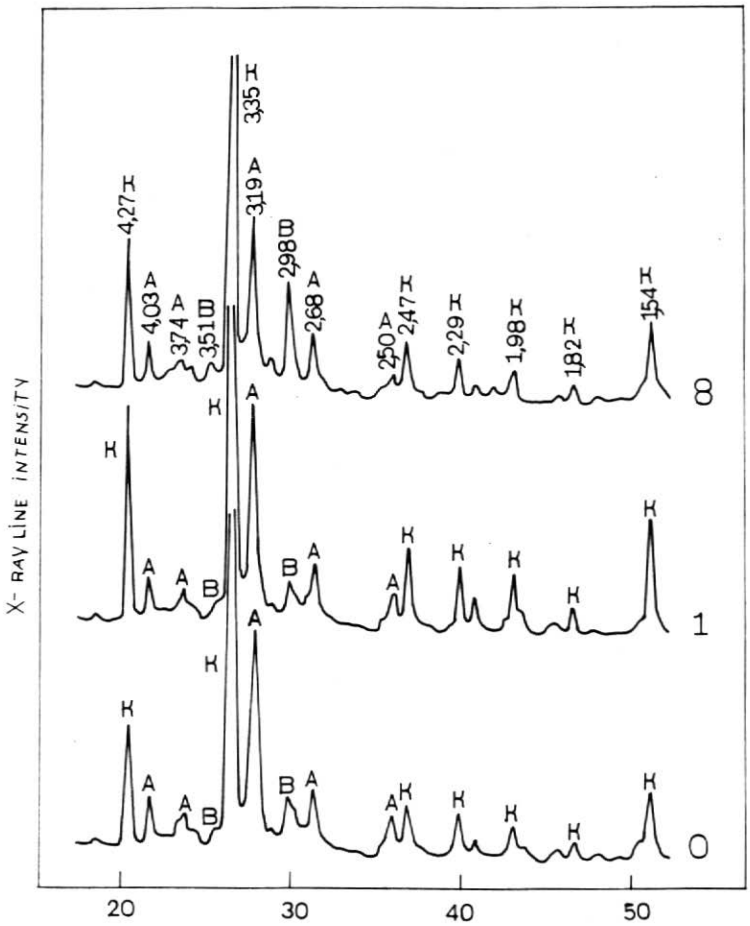

Fig.3: X-ray diffraction patterns from the compositions 0, 1, 8; K-quartz, A-anorthite, B-wollastonite

An electron microphotography of composition 1 is represented in Fig. 4, where the phases which form the ceramic body are seen.

The experimental biscuit bases of all compositions are glazed with conventional cover zircon glaze and are fired at 980ºC in tunnel furnace. The measured thermal stability of wall tiles is above 150ºC and composition 8 possesses the best one - 180ºC. The good results obtained in investigation of experimental series, made possible the successful introduction of kaolin sand as a raw material in production of porous wall tiles. In industrial conditions, two compositions 1,6 were tested:

COMPOSITIONS	1	6
enriched kaolin	20	20
kaolin sand	22	32
clay A	9	2
clay B	12	6
dolomite	10	16
limestone	12	7
biscuit body	12	4
glazed body	-	3
feldspar	3	-

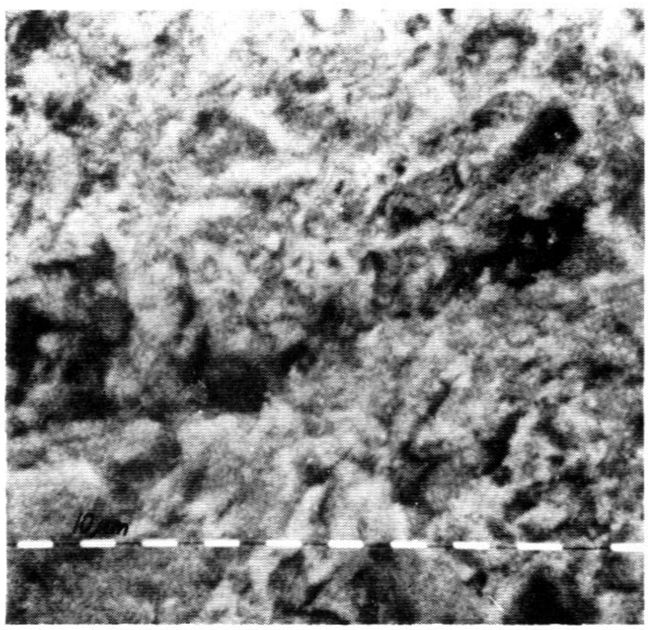

Fig. 4: An electron microphotography of the composition 1

The introduction of two compositions does not change manufacturing parameters of different stages. A variation in wet-milling time was expected, because of the wide granulometric composition of kaolin sand but the process was carried out for 16-18h, which corresponded to present technology.

The characteristics of the obtained wall tiles are represented in Table 4. The data of bending strength confirmed again the favourable influence of kaolin sand on the strength of wall tiles. The other properties correspond to requirements of the present technology. The wastes from biscuit firing strongly decreased - under 5% after the introduction of recipe 1 under industrial conditions, because of the improved strength of biscuit bases. Then recipe 6 was introduced, in which a part of the biscuit waste was changed with a glazed. With this composition is being worked now.

Table 4 Characteristics

COMPOSITIONS CHARACTERISTICS	0	1	6
P-in green state,MPa	0,75	0,79	0,75
P-after drying, MPa	2,41	2,51	2,58
P-after biscuit firing, MPa	14,6	17,5	18,6
P-after glazed firing, MPa	17,8	19,5	20,1
shrinkage, %	0,30	0,35	0,40
water absorption, %	21,8	20,8	20,9
thermal stability,ºC	150	160	170
thermal expansion coefficient $x10^7$, $ºC^{-1}$	60,1	62,3	65,4

CONCLUSION

The compositions of clay ceramic biscuit bases for wall tiles are worked out, with participation ofkaolin sand. An industrial raw material-silica sand is completely changed and the kaolin component is partly changed. It is found out that the biscuit bases are built from anorthite, wollastonite and quartz crystal phases. They ensure a higher mechanical strength for the compositions with higher kaolin sand content.

By means of DTA and dilatometry is confirmed, that the deformation of porous wall tiles depends on the quantity of CaO and on the kind of raw materials, which CaO is introduced by. The dolomite introduction prolongs the sintering range as well decreases the extent of linear variations of biscuit tiles during the heating.

The utilization of a proper kaolin sand quantity in clay ceramic bases, makes possible the obtaining of high quality wall tiles in "Asparuh Company" - Isperih, with daily production 15000 sq. m.

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