Development and Production of Molding Equipment and Plastic masses using new compounding formulations, plastic pressing, drying, high-temperature liquid-phase synthesis and properties of a prototype batch of "yellow" paving stones

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Abstract: *The research is related to the creation of new compounding formulations for the production of "yellow" paving stones. This was necessary due to denied access to a potential source of suitable raw material from the deposit near the village of Svetlen, Popovo municipality. Marlstone raw material from this deposit has the necessary qualities for such production, as a result of which, after high-temperature liquid-phase synthesis, new petrurgic phases with high physicochemical and mechanical properties can be formed. The new compounding formulation of the molding mass was developed on the basis of marlstone sedimentary rock from the Alexandra deposit, located near the village of Lovets, Targovishte district. The use of this compounding formulation makes it possible to obtain appropriate physicochemical and mechanical properties and a yellow coloring equivalent to that of the reference samples.*
Keywords: *"YELLOW" PAVING STONES, SEDIMENTARY ROCKS, PETRURGIC PHASES*

1. Introduction

The first prototype samples of Bulgarian "yellow" paving stones were made on the basis of marlstone sedimentary rock from a deposit near the village of Svetlen, Popovo municipality [1]. Due to lack of access to this deposit, it was necessary to explore suitable raw materials from alternative sources. For this purpose, marlstone sedimentary rocks from the area of the town of Opaka and the village of Lovets, Targovishte district, were studied. The marlstone sediments from the Alexandra deposit near the village of Lovets showed better results [2]. Based on the preliminary analyzes of the raw material and the laboratory samples of the new compounding formulation, an amount of 1 t plastic mass was prepared, sufficient for the production of 100-200 pieces of paving stones which are identical in shape and size to the standard ones. The stages of implementation of the technological regulation from the starting raw material to the high-temperature liquid-phase synthesis of the finished product are as follows: 1. Study of the chemical and mineral composition of the starting marlstone sediment rock in order to establish the presence of an appropriate proportion of individual oxides and minerals; 2. Preparation of experimental samples with modifying additives to obtain the necessary color and optimization of the temperature mode of the synthesis, as well as examination of the obtained experimental samples; 3. Establishing the indicators necessary for the production of molding equipment, such as compressibility of the mass after synthesis; 4. Production of model and molding equipment for pressing the plastic mass; 5. Preparation of the mass according to the established compounding formulation based on sedimentary rock with modifying additives sufficient to form a prototype batch of "yellow" paving stones [3]; 6. Forming process - pressing of blanks from the plastic mass; 7. Drying of the molded products applying an experimentally tested drying mode; 8. Programming and carrying out a number of experimental temperature modes of liquid-phase synthesis until establishing a suitable one, at which well-baked and fault-free paving stones with the required yellow color are obtained [4,5,6]. The researches include mineral compounds, appropriate glass and mineral phases [7,8,9], suitable modifying aggregates [10], etc.

2. Experiments

According to Step 1, a study was carried out on the chemical composition (Table 1), the mineral phases and their percentage ratio (Table 2), and the results of the differential thermal analysis (DTA) of a sample of the raw material heated to 1,140°C with a heating and cooling rate of 3°C/min and isothermal holding of 80 min (Table 3). It was found that the color was darker than that of the reference samples and that the sintering temperature range was 80±5°C. This necessitated the addition of modifiers to lighten the color and extend the sintering temperature range. For this purpose, samples were made with different percentage ratios of modifying additives such as ZnO, Zr2O, kaolin and raw material based on a sedimentary rock whose color lightens when fired. The ZnO samples did not give the required result as they not only did not lighten the color but darkened it even more and did not widen the sintering temperature range; ZrO_2 lightened the color to the required shade but did not stabilize the sintering temperature; the addition of kaolin gave the necessary color and extended the sintering temperature range, but at the same time it also reduces plasticity, thus hindering the molding process. The best results were obtained from the samples including an additive of clays that lighten when fired, such as clays containing mineral phases kaolinite, quartz and muscovite. The chemical composition of the used modifying clay is shown in Table 4.

Table 1: *Chemical composition of sedimentary rock from the Alexandra deposit, Lovets village, Targovishte district.*

Component	Percentage
SiO_2	35.19
Al_2O_3	11.36
Na_2O	0.7
K_2O	2
MgO	2.24
CaO	19.58
TiO_2	0.47
Fe_2O_3	4.85
MnO	0.11
LOI	23.21

Table 2: *Percentage content of the phases of a fired sample of pure marlstone rock only from the Alexandra deposit, Lovets village, Targovishte region.*

Mineral	%
Chlorite	29
Mica (Muscovite-type)	26
Calcite (Mg-containing)	14
Quartz	13
KFs (potassium feldspar)	8
Plagioclase	6.5
Gypsum	2
Kaolinite	1.5

Table 3: *Percentage content of the phases of a fired sample of pure marlstone rock only from the Alexandra deposit, Lovets village, Targovishte region.*

DTA	From MS – dehydration and decarbonization are observed. There are two carbonate phases: the lower-temperature one corresponds to Mg-containing calcite, the higher-temperature phase is calcite. Concerning weight losses, the amount of carbonate phases is about 22-25% The water probably originates from gypsum and chlorite.

***Table 4:** Chemical composition of Ukrainian clay type "Vesko-Prima" that lightens when fired.*

Component	Percentage
SiO_2	63.10
Al_2O_3	31.00
Na_2O	0.30
K_2O	2.10
MgO	0.60
CaO	0.40
TiO_2	1.60
Fe_2O_3	1.00
LOI	8.500

At stage 2, to modify and stabilize the mass, experiments were carried out on test samples with different ratios of chamotte and clay, as well as lightening additives such as ZrO_2, ZnO, kaolin, glass and clay which whitens when fired (Table 5). The best indicators correspond to sample XX with weight parts of clay, chamotte and kaolin of correspondingly 30%, 55% and 15%. This component ratio contributes to achieving good plasticity of the mass, this making it suitable for the molding process of plastic pressing. Residual moisture after vacuum extrusion is 20-25%. The addition of kaolin stabilizes the liquid phase and lightens the mass until a sample corresponding in color to the standard one has been obtained. However, with the addition of kaolin, the mass is still lean, therefore the plasticity is adjusted with the addition of clay that lightens when fired - sample IIa. The mineral phases after synthesis of sample XX (with the addition of kaolin) were studied, and the presence of anorthite, diopside, wollastonite and quartz was established. The mineral phases after synthesis of sample sample IIa (with the addition of clay that lightens when fired) were also studied. Its phase composition is presented in Fig. 1; a DTA was made to establish the temperature mode of sample XX (Fig. 2). The amounts of the modifying additives leading to an equivalent yellow color and high physic-chemical and mechanical indicators were established (Table 5). The mineral composition of the modified samples showed the presence of suitable petrographic phases anorthite and diopside.

***Table 5:** Chemical composition of Ukrainian clay type "Vesko-Prima" that lightens when fired.*

Sample	II	III	VI	VII	XX	IIa
Chamotte	55	55	50	50	30	50
Marlstone	40	40	40	40	55	30
ZrO_2	5	-	5	-	-	-
ZnO	-	5	-	5	-	-
SiO_2	-	-	5	5	-	-
Kaolin	-	-	-	-	15	-
Clay type "Vesko-Prima"	-	-	-	-	-	20

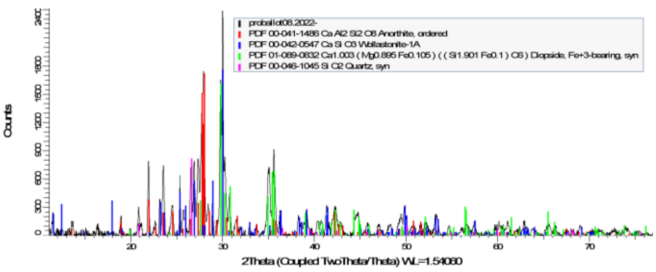


***Fig. 1** Phase analysis of sample IIa with the addition of clay that lightens when fired type "Vesko-Prima", developed in laboratory conditions with the presence of petrographic phases anorthite, diopside, wollastonite and quartz as a result of the modification.*

At stage 3, a firing temperature range of 20-30°C was established, as well as fire shrinkage between 15% and 18%, depending on the humidity of the plastic mass and the sintering temperature. The best results were found for a temperature synthesis at 1130°C, water content in the plastic mass of 20% and fire shrinkage of 17%. A DTA was performed on the modified sample XX with chamotte and kaolin. The analysis indicated several basic steps for sustaining the temperature, on the basis of which experimental modes of high-temperature synthesis were developed (Fig. 2).

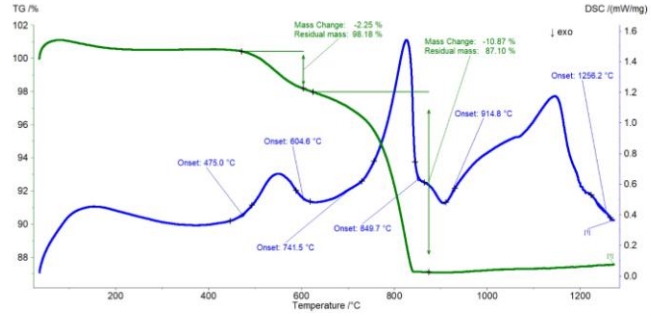
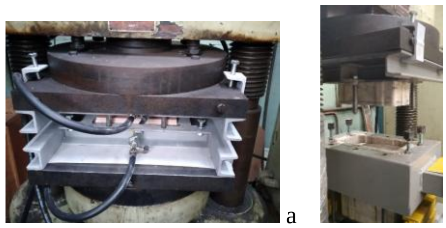


***Fig. 2** DTA of modified sample XX.*

Stage 4 includes the development of model and molding equipment for pressing ceramic blocks of different shape, size and weight, which after sintering acquire a color similar to the “yellow” paving stone standard. Two models were made for molding ceramic blocks with an increase of 17% - a reduced model on a scale of 1:2 and a model in real size. Accordingly, two types of matrix structures were developed for pressing ceramic blocks from plastic mass - one for reduced ceramic blocks (Fig. 4a) and another for block of the original size (Fig. 4b). The two developments differ in their respective constructions as regards their manner of molding, depending on the size of the products. The first one is for pressing reduced-size ceramic blocks and is a metal structure with a mold of polymer modified gypsum mixture that forms the pressing surface. The second is a development for pressing ceramic blocks of the original size and consists of a metal structure and two punches made of composite material which press the mold. Both constructions are proprietary developments and have a number of advantages over traditional matrices, as they reduce the cost of the matrix structure several times compared to an all-metal one. They also have an advantage from the point of view of determining the thickness of the pressed form, adding textures of a decorative and functional nature, etc.



a b

***Fig. 4** View of the installed new matrix structures of the pressing facility: for molding reduced-size blocks in scale of 1:2 (a) and for molding “yellow” paving stones of a shape (b).*

At stage 5, about 1 ton of mass is prepared for the production of a prototype batch of “yellow” paving stones according to the new compounding formulation. For this purpose, the services of external subcontractors were used, as they possess the equipment necessary for obtaining a large amount of mass: a furnace for firing chamotte from marlstone clay, a ball mill for grinding chamotte with a sieve residue below 0.200 mm, a mixer - a ball mill for water grinding and homogenization of a water colloidal dispersion system (slicker), a filter press for removing part of the water content from the slicker, a clay mixer for homogenizing the plastic mass and a vacuum extruder to vacuum the plastic mass. The process of mass preparation is presented in Fig. 5.

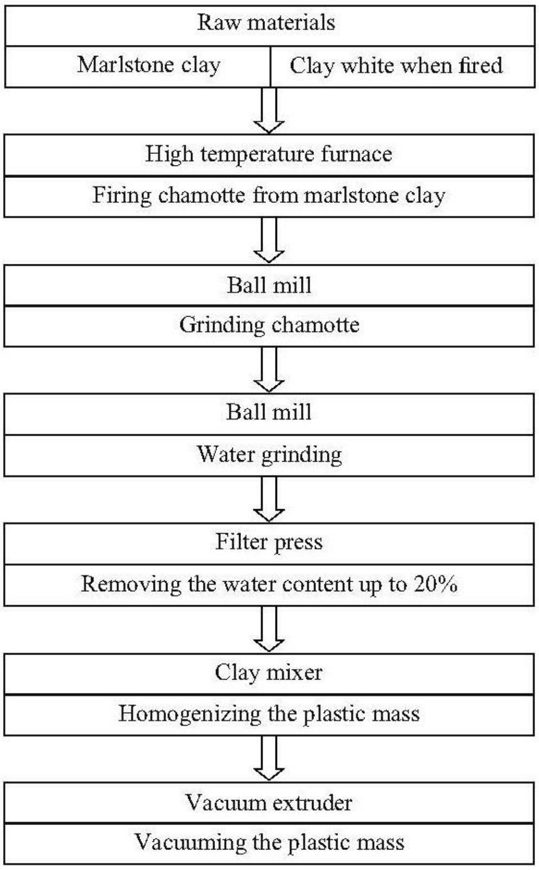


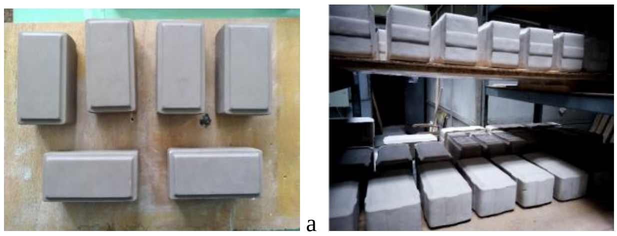
Fig. 5 *Diagram of the preparation of the plastic mass, according to a new compounding formulation, used for the production of a prototype batch of "yellow" paving stones.*

At stage 6, plastic molding is performed. For the reduced-size blocks, the pressing is done using a two-part cast made of polymer modified gypsum. The two parts of the cast split the mold down the middle and form the top and bottom of the product. Separation of the pressed product is done by means of air using a hose installed in both parts of the cast (Fig. 5). With the paving stones of the original size and shape, the process is carried out by pressing the product between two punches. In the metal structure is embedded a negative die, forming the sides of the product, the lower punch forms one front part of the product and presses the mold with a pressure of 13 t/cm^2, and the upper punch sinks 10 mm into the die and forms the other front part of the product (Fig. 6).

Fig. 6 *Molding process of reduced-size ceramic blocks with the following steps: loading with a the plastic mass blank weighing 680 g, pressing with a pressure of 6 t/cm2, successive release of the two parts of the cast by supplying air with a pressure of 6 bar.*

Fig. 7 *Plastic molding process with the following steps: loading a plastic mass blank with a weight of 5.100 kg, pressing with a pressure of 13 t/cm2, separating the pressed product by pushing it out from the lower punch.*

Stage 7 involves drying. The entire cycle lasts no more than 50 hours with a slow increase in temperature from 0 to 100°C for a gradual removal of the water content from the plastic mass and avoiding deformations and destruction of the structure by thermal shock.



a b

Fig. 8 *Dried blocks ready for high-temperature synthesis: a – reduced (in scale 1:2) ceramic blocks and b – blocks of the same size and shape as the original "yellow" paving stones.*

Stage 8 consist of high-temperature liquid-phase synthesis. Various modes were experimented in order to determine the optimal one. Capsules are made to shield the ceramic blocks in the firing process. It was established that the direct radiation of temperature from the heaters causes defects in the structure and deformations of the products with a larger volume and mass. To avoid this, mullite-quartz ceramic capsules are made to screen the products from all sides. With small paving stones, sintering takes significantly less time, due to their smaller volume and mass, and the above mentioned problems in the firing process are absent.

Table 6: *Temperature mode of experimental high-temperature liquid-phase synthesis in furnace No 1 with ceramic paving stones of a shape, size and weight equivalent to the standard ones.*

Temperature mode in furnace No 1				
Step	Temperature, ^{o}C	Retention time, min	Time to reach the set temperature, min	Total time, h
1	100	480	360	14
2	250	240	240	8
3	650	480	360	14
4	850	480	360	14
5	950	120	360	8
6	1130	480	360	14
Total sintering time, h				72
Note:	A 72-hour temperature regime was carried out; 12 paving stones were placed on a plate smeared with Al_2O_3; the furnace embrasures are opened during cooling.			

Results:	Thermal shock probably occurred when the embrasures were opened; stuck to the refractory plates, as a result of which, when shrunk, all have faults, but are well sintered and of good equivalent colour.

Table 7: *Temperature mode of experimental high-temperature liquid-phase synthesis in furnace No 2 with ceramic paving stones of a shape, size and weight equivalent to the standard ones.*

Temperature mode in furnace No 2				
Step	Temperature, ^{o}C	Retention time, min	Time to reach the set temperature, min	Total time, h
1	100	480	360	14
2	250	240	240	8
3	650	480	360	14
4	850	480	360	14
5	950	120	360	8
6	1132	480	360	14
7	1030	20	120	2
8	930	20	120	2
9	830	20	120	2
Total sintering time, h				72
Cooling time, h				6
Note:	The samples are screened from above and below and placed on a thin layer of Al_2O_3 powder (with a grain size greater than 120μ); with three steps of cooling; A temperature mode of 72 hours sintering and 6 hours cooling was carried out.			
Results:	Good scrap, well sintered, holds its shape, does not stick, deformed by its own weight on the side it lies on - most likely the temperature is 2-4°C higher.			

Table 8: *Temperature mode of experimental high-temperature liquid-phase synthesis in furnace No 3 with ceramic paving stones of a shape, size and weight equivalent to the standard ones.*

Temperature mode in furnace No 3				
Step	Temperature, ^{o}C	Retention time, min	Time to reach the set temperature, min	Total time, h
1	100	480	360	14
2	250	240	240	8
3	650	480	360	14
4	850	480	360	14
5	950	120	360	8
6	1128	480	360	14
8	830	20	450	7.5
9	100	5	900	15
Total sintering time, h				72
Cooling time, h				22.5
Note:	2 pcs. shielded from the top, sides and bottom placed on a thin layer of Al_2O_3 powder (with a grain size greater than 120μ); 1 pc located on the side unshielded on a refractory plate sprinkled with a thin layer of the same Al_2O_3 powder.			
Results:	The unscreened sample is cracked at the bottom and with a large deformation; the shielded samples are cracked at the bottom and have a small deformation - they retain their shape, have a good color, are well sintered. Conclusion: To switch to sintering in capsules.			

Table 9: *Temperature mode for sintering of ceramic blocks reduced at a scale of 1:2 compared to the original ones.*

Temperature ^{o}C	Retention time, min
150	60
650	60
840	180
1140	180

3. Conclusion

The new composition based on marlstone sedimentary rock from the Alexandra deposit, located near the village of Lovets, with added chamotte from the same raw material and clay that lightens when fired, shows good molding capabilities for pressing both reduced-size paving stones, as well as paving stones identical in size, shape and color to the reference ones. The experiments carried out cover a complete process for making a prototype batch of “yellow” paving stones. Additional tests should be done on samples of the newly obtained products, such as X-ray phase analysis, petrographic analysis, structural analysis with computer tomography, tribological tests for wear against various contact bodies, etc.

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