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## A method for the production of thermosetting polymeric composites

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*It is offered to carry out the thermoreactive polymer composites polycondensation process in the kinetic reaction mode with removal of by-products due to reactive diffusion. The method can reduce the processing time, energy consumption and increase the productivity at least by 10 times and in future it can be used with success for production of high-temperature ceramics – in "soft" conditions, at temperatures within 200 °C.*

**Keywords:** thermoreactive polymer composites polycondensation, phenolformaldehyde bond, high-temperature ceramics.

### Introduction

The composites, in which matrix (the binding substance) is a polymer component, are among the most numerous and different types of materials in a variety of areas of human technological and household activities. The use of polymer composite materials (PCM) in different areas gives significant economic benefits and different improvements. The intensive development, high efficiency and wide areas of composites use, the domination of their use [1 – 4] allowed academician A.A. Berlin, one of the leading experts in the field, to suppose that the 20<sup>th</sup> century can be symbolized as the "polymer century".

The composition and structure of different PCM are extremely various. It is due to the demand and the continuing efforts of the engineers to improve them. The first classification divides composites to thermoplastic and thermoreactive [1]. Thermoplastics of ordinary use (household, additional machine and device components, etc.) as a rule are inferior to thermoreactive PCM with their operational characteristics of their use in extreme mode of exploitation. The latter must usually possess high strength, high-temperature and heat-resistance [5]. However, the production cost is extremely high, and the technology is very temperature-dependent. Only metals and their alloys can compete with them in this regard.

As the fibred PCM matrixes, the thermoplastic high-heat resistant polymers were made and developed and now they are applied. These are the so called "superstructural" plastics: polyethersulfone, polyetherimide, polyphenylene sulphide, polyetheretherketone, etc., with high parameters of mechanical stability and heat-resistance enduring high temperatures [5]. However, the production cost is extremely high, and the technology is very complicated. That's why the thermosetting materials have not lost their importance.

Moreover, such "archaic" materials as PCM based on phenolformaldehyde binding substance (of polycondensation genesis) do not step back [6]. They have been successfully used in many types of products, for example, for the manufacture of molds in the steel industry, as ablation of one-use products for heat protection of missile heads and spacecrafts [7, 8] and in the production of processing, grinding tools [9, 10].

About 50% of abrasive products in the world is manufacturing using organic binding substance, mainly, phenolformaldehyde one. Some manufactures from huge transnational corporations ("Tyrolit", for example) developed some modified materials for their products that improved the operational characteristics of the abrasive tool. But the price of these products is several times higher than the price of their analogues made using phenolformaldehyde matrixes. Therefore,

taking into account the ratio of price - quality, many of the major Western European consumers often prefer to use the product based on phenolformaldehyde. And it is practiced even by companies of the countries in which production using phenol formaldehyde is prohibited by law - for environmental reasons: through the tool export from other countries (where production is allowed).

PCM with phenolformaldehyde matrix and products made of them have both important advantages and significant disadvantages. [4]

### The advantages are:

- 1) Good technological properties: low viscosity of the binding substance, good wettability and saturability of armor material, comparatively low temperatures of hot-setting (160 – 200 °C);
- 2) Good adhesion to most filling materials and functional additives;
- 3) Increased heat resistance;
- 4) Stability in different environments: chemical, hydro- and exterior resistance, low permeation for liquids and gas;
- 5) PCM properties can be regulated technologically in the wide range varying the components, adding modifiers, catalysts and changing the hot-setting (solidification) conditions.

### The disadvantages are:

- 1) Fragility, low fracture toughness and low impact resistance, strength (they even get worse for high heat resistant matrixes);
- 2) Long time of the hot-setting (solidification) caused by the necessity of exothermic chemical reaction carrying out in the "soft mode" (without significant overheating);
- 3) The lack of appropriate ecological safety – both of technological process by open method (due to the release of volatile fluids phenol, formaldehyde, etc.) and the manufactured products.

The aim of this study was to radically overcome these disadvantages, and in the first place - to achieve dramatic reduction in the duration of the curing process (hot-setting process duration) and to achieve significant environmental safety as the manufacturing process and its products.

The research was of experimental character. As the object of improvement the author has chosen the technological process of abrasive tool manufacturing based on phenolformaldehyde binding substance. This was because of the considerations that this type of abrasive tool products from PCM is widely recognized as the most difficult subject for innovation. This "complexity" in this case is caused by the necessity to find absolutely new combinations of input parameters of the

process for any technological modifications. And with the adding of abrasive material into composite a number of factors such as dynamical forces at short-term heating up to 500 – 1000°C (while using the products), appearance of possible – side and undesirable – tribochemical effects must also be taken into account. However, composite, made for abrasive purposes, can immediately be safely used for other needs (e.g., structural purposes), without special technology efforts and new developments.

### Elementary model of the process and its modernization

#### 1. General knowledge of getting polycondensation materials PCM

The procedure of product manufacturing made of PCM with phenolformaldehyde matrix is as following. The macrohomogeneous mixture of different dispersed filling materials and armor elements, of initial polymer resin-binding substances, modifiers of functional binding material groups and also some special components (abrasive nuclear, in particular) is made.

Thermoplastic resins, such as pulverbakelite (novolac with aminoform additive) with liquid bakelite (low-molecular oligomer of resole type) are used as a binding substance [1 – 6, 10 – 12]. The mechanism of aminoform action to change novolac into the resins with resole properties is well known [13]. Liquid bakelite is used for the maximum charge stock homogenization [10]. Various materials are used as filling ones [9 – 11]. Molding of this mixture is made under the pressure of 60 – 200 MPa to get the blank of suitable standard size. Finally, the baking (or sintering) takes place – directly in the compression mold or out of it (in special kiln of tunnel type or intermittent action). “Hot” molding (in the compression mold with a heater) is the quickest: the product of medium size hardens during 2 – 3 hours. The quality of this composite is always high. But this technology is used mainly for carrying out of special single-piece orders because it is non-profitable: you can get only one unit at one baking. At “cold” molding and baking by open type about a ton of units can be hardened during one cycle of baking. The cycle of baking, in this case, is much longer. It is ever longer for large-size units. For example, for providing of the necessary degree of matrix polycondensation (it is defined by the required levels of physical-chemical parameters of a unit) the baking of abrasive cutoff disks with the diameter up to 230 mm (at the height of approximately 1 – 5 mm) in the kilns of intermittent action lasts approximately 16 – 24 hours. The baking of larger units takes approximately 70 hours (it depends on their size). As there are several avoidable physical-chemical reasons of such an excessive duration of the process we will analyze the situation more simply to find the means of their avoidance.

A huge amount of literature on the subject and some practical experience of the author [14] show that neither the used (inert) filling materials of PCM units nor often used element-organic coupling agents and modifiers of matrix reaction-able functional groups (chemical, structural and copolymers) can be the reason of “slowness” of the process as a whole. Hence, this reason is in the process of polycondensation, in the reaction of phenolformaldehyde matrix formation.

Genetically, the formation process of polycondensation PCM matrix begins with the reaction of the initial phenolformaldehyde obtaining from phenol and formaldehyde (with H<sub>2</sub>O exhalation) by a well-known scheme. The formation of the stable matrix goes through the steps of polycondensation

and changes of the following type: Resol (flux, low viscous up to 120 – 130°C resin) – Resitol – Resit (high viscous up to 130 – 200°C environment) [2]. Polycondensation - the connection of many molecules (monomers) or blocks, accompanied by low molecular substance removal of them: for example, water, hydrogen chloride, ammonia, carbon dioxide, etc. [16]. The monomer molecules or their blocks, incorporating at least two functional groups – Y and Z, and capable to react with each other, take part in polycondensation. Sometimes the mixture of two monomers (monomer blocks), one of which contains Y groups on both ends of the molecule, and another – Z groups, is polycondensed. Flory allowance [2], that the reactivity of reaction groups Y and Z (potentially) does not depend on whether they are composed of monomers or units (polymer chains) of any length, is usually accepted.

Finally, it should be noted that both functional groups Y and Z are present during the polycondensation process of the “bakelite” ligament of all phenolformaldehyde blocks. The role of one of them the group CH<sub>2</sub>-OH performs, and the other - a hydrogen atom H, located in the ortho- position with respect to OH in the benzene skeleton. Moreover, the possibility of interaction of Y and Z groups (not Y and Y, or Z and Z) is ensured with the dynamic change in the relative conformation of groups – as the result of their inductive interaction. As a result of the elementary acts of two polymer block joining, the water molecules are formed which is the most important for our further discussion. Fundamentally, it is very important that every virtual monomer (a pair of the newly formed valence ligaments) taken part in the process of this composite macromolecule formation forms the by-product – a water molecule.

#### 2. The specifics of the negative role of reactive “volatile” by-products

While increasing the polycondensation degree (with nucleation of new macromolecule blocks and their cross-links with the analogous macromolecules) the amount of H<sub>2</sub>O number increases monotonously. This leads to the metastable state at a certain moment of technological increasing of the temperature. The metastable state leads to the polycondensation inhibition and even to the process termination, up to the matrix destruction because of the main reaction reversibility [16, p. 147 – 150; 17]. This presented situation will be even worse if polycondensation is considered not in the formal-analytical aspect of a chemical reaction but in its top chemistry aspect. In fact, all the monomers forming the macromolecule gave their water molecules at the condensation of the primary monomers and at the ligament formation in the Resite structure. Water, from elementary considerations, has no normal conditions for co-crystallization [18] (high temperature) or for co-precipitation [19] within the already polycondensed part of the matrix. Therefore, during the process, H<sub>2</sub>O continually pushed back, “squeezed” out of macromolecules - rising to the surface of the growing high-molecular blocks.

Dispersion factor, the block surface area (as the ratio of their surface S to the volume V) decreases with the increase of the characteristic size of the block r by hyperbolically law:

$$S/V = 1/r$$

That is, the number of active single “monomer” of bonds per unit surface of the growing unit, reduced by the same law.

But the number of the displaced (in this area) of water molecules on the contrary - increases proportionally to the reacted volume:

$$V = r^3$$

In other words, the number of water molecules per active ligament, will increase proportionally to  $r^2$ : if, for example, if the unit will increase by 3 times the amount of the hydroxyl groups blocking the ligament will increase approximately by 10 times. In the concepts of the absolute response rate theory this "blocking" is described very clearly [20]. Reaction rate constants, it should be determined not on the basis of the volume but the surface concentration of the initial and final products. Thus, case, the Flory allowance absolutely cannot be satisfied in this situation. With increasing molecular weight of the main target of the product the viscosity of the reaction medium increases, the mobility of the formed macromolecules decreases and the removal of by-products becomes difficult. Their excess definitely can dramatically shift the reaction to the left. That's why at the manufacture they try to carry out the polycondensation at the high temperature at first (to achieve the high speed of the process), and then they reduce it at the approach to equilibrium position – to get the product with larger molecular weight. All those long, long exposure at some intermediate temperatures significantly lengthen the process. Molded under pressure 60 – 200 MPa for further firing (sintering) mass PCM is essentially heterogeneous system. In the case of production of abrasive products this is a macro-homogeneous mixture of grains, filling material and polymer binding substance. The latter turns into the molten state and saturates the whole system semi-uniformly before hardening. That's why the hardening of the binding substance looks like the crystallization from the solution-melt [21] and has the character of the so-called "mass crystallization" that is, should, apparently, occur simultaneously throughout and very fast - in a matter of seconds [22]. In reality, polycondensation occurs over many hours or even tens of hours (in the production of large-sized products). - The question is, why?

It is believed that the polycondensation is like a crystallization growth on the set of "priming" polymer blocks (embryos, crystallization centers) [23]. Such a heterogeneous process is characterized (like a crystallization process) by the inherent set of physical-chemical effects and specific sequence of stages of their appearance [21, p.124, 24], the transition from the initial stage to the final state (which in our case is the hardened polymer-ligament) These stages are different: the embedding of the "crystallizer" in the structure, the sorption – desorption of initial source and by-products, the diffusion of both. All these stages are divided into 2 groups: kinetic and diffusive. Since the process is complex, it is limited by the speed of the phase formation and is entirely determined by the slowest of all the stages. In this sense, each of these stages can be described quantitatively - their own rate constant "k". The process occurs in the "diffusion" or "kinetic" regime [21], depending, respectively, which of these constants, the smallest (in principle very rare "intermediate" mode is also possible).

The concept of "kinetic resistance" R of the heterogeneous process can be introduced as the ratio [21, 22]

$$R = 1/k \quad (1)$$

So, the observed (real) resistance  $R_{\text{observed}} = 1/k_{\text{observed}}$  is equal to the sum of the kinetic resistance of individual stages of the process [21]

$$1/k_{\text{observed}} = 1/k_k + 1/k_d, \quad (2)$$

where  $k_{\text{observed}}$  - is a constant of the total (observed) process rate;  $k_k$  is a constant of kinetic stage rate;  $k_d$  - is a constant of diffusion stage rate. It can be shown that  $k_d$  is similar to dif-

fusion coefficient D [24, 25]. Literature about polycondensation of phenolformaldehyde compositions (bakelization) [1, 2, 3, 9, 10] clearly indicate that the bakelization (by the known methods) is carried out in the diffusion regime. In this case, the nature of the diffusion is the removal of the reaction and capillary water, which excludes the presence of an acceptable sufficient degree of polycondensation. The author ascertained this trivial facts previously through own experience [26]. The important distinctive feature of polycondensation reactions is their reversibility. In other words, they do not get to the end at ordinary conditions (for example, in a conservative system), and the chemical equilibrium of the products and initial reagent is established in the system. For as the reaction in the system accumulate low molecular weight by-products (water, etc.), which shifts the equilibrium of the process to the left. It is for this and only for this reason that produced by traditional methods polycondensation polymers have a much lower molecular weight than the polymerization (respectively,  $\sim 10^4 - 10^6$  units and up to 50,000 units). [16] The escaping by-products ( $H_2O$ , in particular) can cause the partial destruction of the forming polymer which can thus partially decompose – up to the initial substance. As a result, as many active "external" ligaments already formed macromolecules will attach to new monomers (blocks), as they will be released from  $H_2O$  presence.

For any order kinetics of polycondensation the first addend in (2) is insignificant, and the duration of the definite new block formation can be compared in magnitude to the period of the nucleus and electron vibrations in the molecules [20]. To provide the high rates of polycondensation the general growth resistance R should be reduced essentially by providing the best high values  $k_d$ . It is not provided in the real life: the process is really slowed-down as a whole. As already mentioned, the block polycondensation is carried out at the diffusive mode. The physical – chemical essence of this mode is the extremely long volatile diffusion (they released during polycondensation to 20% by weight [9, 10]), - mainly water - through the composite volume outside of the product. This process is extremely slow, as the diffusion in heterogeneous systems of this kind is the subject of the unalterable rule such as Fick's rule [24]

$$M = DF \Delta C \tau \delta^{-1}, \quad (3)$$

where M – is the quantity of the already diffused substance, kg; D – diffusion coefficient,  $m^2 \cdot s^{-1}$  (according to the Stokes - Einstein's equation  $D = k_B v^2 / \eta$ , v is the kinematic viscosity [24]); F - is the surface area through which the diffusion is taking place,  $m^2$ ;  $\Delta C$  - is the change of the layer concentration with the thickness  $\delta$ ,  $kg \cdot m^{-3}$ ;  $\tau$  – time, s;  $\delta$  – the layer thickness through which the diffusion is taking place ("diffusive way").

Partially polycondensed medium PCM with the filling is the continuum close to the properties of the solid. Therefore, for the assessment calculation can be considered [24, 25]

$$D \approx 10^{11} - 10^{12} (M^2 \cdot s^{-1}).$$

At characteristic values of  $\delta$  proper to the typical sizes of abrasive units [1], it gives the values  $\tau > n10$  hour (n – is an integer, always more than one) for bulk-volume typical sizes. It corresponds well to the realized durations of the bakelization processes of the abrasive-instrumental units: approximately 16 – 24 hours for small sizes (tear-off) discs 125 – 230 mm in diameter, and 2 – 3 days for bulk-volume units 150 – 300 mm and more in diameter and more than 6 mm in height.

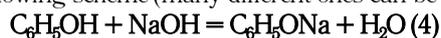
$H_2O$  molecules, diffusing from some local microvolume of

PCM immediately replaced by similar molecules to enter this microscopic volume (due to the same diffusion) of the neighboring zones (similar to micro volumes). The situation of the prolonged "inhibition" of the activated complex [20] is partially realized near the area of each polycondensed block enlargement. It is realized partially because the equilibrium is moved to the polycondensation while the diffusive outlet of water out of the object borders. In spite of the gradual diffusive outflow of water to a greater or lesser extent, the situation continues to maintain chemical equilibrium with the lack of a complete shift of the reaction to the right.

The situation becomes more complicated (in terms of additional prolongation of bakelitization period) especially when you consider the actual process of heating produced products. Their heating up is carried out (both in the special kiln of tunnel type or intermittent action [9]) "outside": the external zones of large products for a long time have a higher temperature than the inside - from the known laws of physics of the total thermal conductivity. Therefore, the concentration of water diffusion ("out") is imposed the opposite direction ("in"), the driving force of thermal diffusion [25]. This in an unsuccessfully chosen heating modes (for example, very fast) sometimes leads to the formation of PCM products in a kind of hydrothermal clusters (moisture), and the consequence would be a "swelling" [9, 10], it is the destruction of goods, products defect. There are situations when the intermediate process control reveals a high degree of polycondensation of the outer layers of the product and low - internal. So, that is why the existing traditional technology polycondensation RMB have a significant disadvantage - excessive duration of the sintering process. In the framework of the existing well-known method it is impossible to reduce the duration of polycondensation essentially and determinately.

### 3. The basic principles of the offered modification of the process

Equation (2) demonstrates that the rate of polycondensation is essentially unique ("fatal", one might say) and it is determined by the rate of outflow of water: slow flow - slow polycondensation. Other by-products do not do any good for the process too. About 20% of volatiles [9, 10] water, superfluous (free) phenol, ammonia (injected into the ligaments as urotropine to initiate the start of polycondensation), etc. - are removed from the system during the cycle of a unit solidification. As is well known in organic chemistry (and, it is widely used in the analysis to determine the content of free phenol resins) [2], free phenol can be easily removed from the reaction by transferring it to the solid compound with an appropriate solid additive to the filler of the  $M(OH)_n$  type - using the following scheme (many different ones can be found):



though some more water is removed during this reaction. The ammonium is supposed to be removed by the same way. It appears, therefore, that the main "problem" creates water - condensation (capillary) and reaction water. So at the beginning of research on the subject by the author of this work in the first place was decided to remove the condensed water from the initial polycondensation products. [26] It was carried out at the stage of raw materials preparation by different methods: for example, drying the liquid bakelite (BG-3) with different water absorbents of NaA, Na-Y zeolite type, dehydrated by heating  $CaSO_4$ , borax,  $MgSO_4$ , NaCl, etc., which in principle can be re-used and regenerated. The increase of the polycondensation degree and the reduction of the baking

duration were achieved. Therefore, the results of studies [26] immediately inspired the author to develop the identical technique for the withdrawal of the polycondensation and reactive  $H_2O$  from the phase space of the polycondensation reaction.

To speed up the process of polycondensation in PCM significantly is possible only by transferring the process from the diffusive to the kinetic mode. There is no any other way. But the only way to do this is a sharp acceleration of diffusion processes, that is, the intensification of removal of by-products (in this case mostly water) from the zone of the polycondensation process - that is, it would seem, of the total product. It is interesting that it has not been taken into account during many decades of the technology development. There are many references where some qualified authors describe how they tried to quicken the polycondensation process in abrasive products using the exactly same method [9 - 12].

Fortunately, there are many solutions of the original problems of thermal and mass transfer at the conditions of extreme kinetic difficulties [28, 29]. There are many mechanisms and varieties of diffusion process and they can be managed in one way or another - creating the desired mode of mass transfer. In particular, there is the so-called reactive diffusion besides the concentration and thermal ones. Its essence is as follows. If the substance A diffused through the material, in general, the heterogeneous system, substance (phase) B is included into its structure, at the suitable structure and external thermodynamic conditions A and B can chemically react with each other to form a new, strong solid phase - for example, AB.

Several phases of varied and complex type can be formed in real conditions. However, the appearance of a new phase leads to significantly accelerate the completion of the diffusion process - generally due to 2 reasons:

- reducing the diffusion flux (up to its complete termination) because the diffusive chemical particles are connected with the stable chemical particles of the medium through which diffusion occurs,
- increasing the thickness of the separating layer of a new phase, which in this case has much lower diffusion coefficients, which makes the movement of the moving particles in the environment difficult.

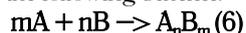
Theoretical analysis of reactive diffusion processes, in general, is incredibly complex, and for multi-component and multi-phase systems of our type now is generally impossible. Frankel and Sergeev [20] gave a model for the formation of intermetallic compounds such as  $A_nB_m$  type for the A atoms diffusion through the B substance (the reciprocal diffusion takes place in general case). It is determined that the transfer of A diffusion front along some axis  $X$  obeys the following law:

$$x = k(Dt)^s \quad (5)$$

Thus, the speed of reactive diffusion (provided that the diffusion coefficient is stable and is  $D \approx 10^{11}-10^{12}m^2c^{-1}$ ) is several orders (p) higher than the speed of concentration diffusion. Remember that  $D^{1/2} \approx 10^D$ ,  $p > q$ . It is determined that the given parabolic law (5) is correct for the general case of solid solution formation due to the reactive diffusion [15].

In case of polycondensation during PCM baking the crystal (reactive) water is the "diffusant A" and it is desirable to reduce the duration of its diffusion by several orders. In other words, it is necessary to introduce into the filling, uniformly distributed between the ligament particles in the forming mass, some substance B that in the polycondensation

temperature mode forms the solid compound of the  $A_nB_m$  type by the following scheme:

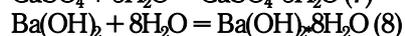
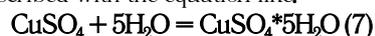


In turn, compound  $A_nB_m$  in this case is intended to act as a sort of additional, already "passive" filler, which successfully fulfill the role of the regular PCM fillings. Passive fillings are traditionally used in the production not only abrasive, but constructive PCM [2, 3, 9, 10].

The duration of  $H_2O$  reactive diffusion by the scheme (6) can be several times less than the observed in the existing processes of concentration diffusion in polycondensation – because of the fact that the duration of diffusive way  $\delta$  (is a part of (3) correlation) can be reduced dramatically by the introduction of "B", and significantly more than an order of magnitude. Indeed, bearing in mind the specific abrasive products for "bakelite" ligament, their baking the characteristic value of  $\delta$  is from some millimeters ( $n \cdot 10^3$  m) to some dozens of millimeters (according to the minimal product sizes). If one introduces a dispersed element B into the homogeneous medium, then the reactive diffusion in the same situation the value of the diffusion path does not exceed the values of  $\delta < (4 - 5) \cdot 10^5$  m. This is the regular order of the recommended dispersity of the powder-like fillings [9]. In our case it relates to the additive component in the role of a substance B in the correlation (6). That's why the possibility to decrease the duration of the regular process of phenolformaldehyde composite baking at least an order of magnitude is real.

It remains to examine the composition, structure, and in general the nature of what is necessary to accelerate the process of substance "B". Recall that B should give a solid connection with the water, which in our treatment was designated as a compound of "A" (see correlation (6)). The compound  $A_nB_m$  should be formed, where A is water.

As is known, liquid and solid substances forming at the hydration (joining water to them) of simple substances and also salts, acids, bases and organic compounds are called by hydrates. For example,  $CuSO_4 \cdot 5H_2O$ ,  $Ba(OH)_2 \cdot 8H_2O$  and some other. They are solid crystal substances (crystal hydrate) [30] each molecule of the main substance in them can have up to 24 water molecules, for example, chrome-potassium sulfate  $Cr(SO_4)_3K_2SO_4 \cdot 24H_2O$  [31, p. 130]. The joining of water at the reaction scheme (6) is called hydration and is described with the equation like:



In our work, finding the method of the speeded up polycondensation of PCM matrix besides the use of the compounds of the mentioned type (several dozens of compounds and their combinations were approved), the high-temperature (not dying at their functioning up to 1600°C) high-aluminous cements, zeolites and molecular sieves of different type [32] based on them were used.

Taking into consideration the 'abrasive' application an important criterion for selecting potential adsorbents (in the reactive diffusion  $H_2O$ ) was their heat resistance, stability. As the result of the thermal analysis, the high heat stability of zeolites from the clinoptilolite class was determined [32, 33]. At atmosphere pressure the heat stability of the regenerated zeolite as the ability to absorb water from the environment appears up to 200°C, you should pay special attention in the light of its use for our purposes. Moreover, under pressure (even slightly above atmospheric) and in the compressed state (in particular, after forming of phenolformaldehyde type PCM mass in the filling) this ability to absorb and retain

water, is apparently maintained until at least up to 700 – 900°C. It was proved experimentally: the products with absorbent fillings sustain the temperatures up to 900°C successfully.

"Crystallization" pressure (general ligament coordination) greatly increases the balanced temperature of dehydration (as far as its increase from 500 – 600°C). According to the literature [31], reactive (reagent grade, highly pure) hydrated magnesium sulfate should completely lose all seven water molecules is at 200°C. However, if you take very thick layer of the substance (10 – 15 cm), the dehydration cannot be reached even after 2-hour baking at 350°C. In the compressed state (under the pressure of  $P = 140$  MPa) in the mixture with phenolformaldehyde ligament magnesium sulfate does not dehydrate even at  $T \approx 700^\circ\text{C}$ . At the same conditions calcium sulfate  $CaSO_4 \cdot 2H_2O$ , barium oxide hydrate  $Ba(OH)_2 \cdot 8H_2O$ , chrome-potassium alum, nickel and zinc sulfates, and many others behave analogously or even stricter. Note:  $Ba(OH)_2$  is very heat stable as a sorbent and continues to absorb water at the temperatures of several hundred degrees even at the atmosphere pressure, it loses water only at temperature higher than 700°C. The analogous stable increase of the temperature of dehydration (at the embedding in the PCM structure) was shown by the iron-ammonium alum  $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ , cobalt sulfate  $CoSO_4 \cdot 7H_2O$ , copper sulfate  $CuSO_4 \cdot 5H_2O$ , sodium tetra borate  $Na_2B_4O_7 \cdot 10H_2O$ , chrome-potassium sulfate  $Cr(SO_4)_3K_2SO_4 \cdot 24H_2O$ , zeolite Na –  $YnH_2O$ , zinc sulfate  $ZnSO_4 \cdot 7H_2O$ , pyrophyllite  $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$  [33], high-alumina cement (HAC) HC-75 (was tested in the combination with other crystal hydrates as a filling) and many others. Several dozens of the compounds were tested. Some of them were rejected as defective because of geometrical and structural discrepancy to the chemical composite structure. However, these obtained samples of the composites are suitable for use in constructional purposes.

### Experimental Section

The offered method of the carrying out of polycondensation was reliably verified experimentally: during 2 – 2.5 hours of baking (instead of 24 – 70 hours) several hundreds of samples of material and products in the form of abrasive cutting and grinding wheels where received. That fully complies with product standards and operating parameters and exceeds the working requirements of the Soviet Union State Standard by 2 – 4 times. And this despite the fact that the author did not try out a technology as such, but it is only "method", his marketability. Testing of "technology" usually is to control the hardness of the composite (by the additives and forming pressure variation), optimization of the charge component correlation, glaze introduction and many others. It is a very hard work with dozens of experiments. Instead of these experiments, the author tried to extend widely the number of the real crystal-hydrate additives to the charge.

The combination of industrial pulverbakelite SPF-12A and liquid bakelite BG-3 [34] was used as the binding. Thoroughly dehydrated by heating crystalline filler was either part or entirely replaced it. The electrocorundum normal and silicon carbide (fractions used in the typical production of the products of the same typical sizes) were used as an abrasive particle. Formation of our units (series of 11 – 12 cutting wheels or 3 – 4 grinding wheels of larger sizes) was held simultaneously with the formation of the off-the-shelf items of the same kind: on the same presses and by the same operators. After that the units in the special typical metal cassettes

were placed into the shop intermittent oven with the large group of the typical intermediate products. In initial experiments, the heating was up to the secure temperature (- 195°C) during 2 – 2, 5 hours. Then the samples were kept in the kilns for 2 hours. But, it turned out that the achievement of the limiting temperature (during 2 – 2, 5 hours) was enough to obtain a full polycondensation in the samples. Then the whole truck with the bulk of product was wheeled out of the oven, the experimental samples were taken out in the hardening mode, the industrial part was wheeled back into the oven where it was heated (for more than 20 hours, often for more than 70 hours).

The comparative weighing of samples (preprets and their products), the solidity determination (hardness test) – by Rockwell and Brinell, and also by the industry accepted acoustic method [10, 35] and by frequency meter of natural vibrations “Sound – 107-02” were made. The break testing of all the products was made using the official method [36] on the plant centrifugal testing machine of the one compartment model SIP-800. The cutting value (or grinding value)  $K$  of the experimental cutting abrasive instruments was determined using the official method [10, etc.] – cutting the 10 – 20 steel switches with the diameter (usually) of 25 – 30 mm and calculating by the formula  $K = V_m / V_k$  ( $V_m$  – is the total volume of the cut-off metal,  $\text{mm}^3$ ;  $V_k$  – is the volume of the wheel grinding off). The product abrasion stability was controlled selectively. The stability and the grinding coefficient of the wheels were not tested because of the absence of the express (faster) methods (not going beyond the other mentioned characteristics). These coefficients are determined during the operation process of the product by the consumer by the existing industrial tradition.

All the obtained experimental products have the increased smoothness and perfect texture of the surface, chips and sections – corresponding more to the analogues obtained at hot molding. The best samples have the “classical” bakelite colour: from light to dark brown. Their mass and density surpass these characteristics of the typical products by 18 – 20%: the unit and polycondensed product mass were practically the same. This fact is enough to think about the realization of the maximum polycondensation and enough to suggest the implementation of a maximum of polycondensation. All the “volatiles” are in the structure. The fact of crystal-hydrate “submatrix” formation is easily identified with the IR absorption bands referring to OH groups (normal vibrations of simple and compound forms). The hydration process at polycondensation is clearly seen at DTA curves (differential thermal analysis) with the known methods used in this work [12]. Water is the perfect chemical transporter. That’s why its chemical adsorption prevents positively from the absorption of other dangerous products (that can be separately chemically adsorbed). It raises the “ecological compatibility” of the process. The high degree of polycondensation and crystal-hydrated submatrix (the capsulation in a way) raise the reaction stability of the product to the external action. For example, the introduction of the additive of the “dead-burnt” gypsum (its long heating at 300 – 400°C) leads to the absolute insensibility of the product to the moisture: 24-hour product exposure in sea and fresh water only raises their grinding coefficients.

In the end we can give some examples on the speeded up unit baking.

### Example 1

Cutting wheels 1-230x3xx22 – experiment series “ $\alpha$ -IV” (the symbols are conventional).

Charge (mixture): electrocorundum normal 63H – 40H (70:30%) – 2,5 kg; BG-3 – 0,14 kg; SPF – 12A – 0,35 kg; magnesium sulfate  $\text{MgSO}_4$  – 0,5 kg; gypsum dead-burnt – 0,08 kg. Polycondensation is 1 hour 50 minutes. The testing results (10 products): solidity (acoustic method) SM2,  $K = 3,6$  (steel stick with the diameter of 25 mm, the duration of sinking – 3 seconds).

### Example 2

Cutting wheels 1-230x2xx22 – experiment series 23a (the numbers are conventional)

Charge (mixture): electrocorundum normal 63H – 40H (50:50%) – 2,5 kg; BG-3 – 0,13 kg; SPF – 12A – 0,35 kg; magnesium sulfate  $\text{MgSO}_4$  dehydrated – 0,15 kg; calcium phosphate  $\text{Ca}_3(\text{PO})_2$  – 0,02 kg. Polycondensation is 2 hours. The testing results (12 products): solidity ST2 [10], cutting off coefficient  $K = 3,4$  (round section steel stick with the diameter of 25 mm, the duration of sinking – 2,7 seconds).

### Example 3

Cutting wheels 1-230x3xx22 – experiment series “C-31”

Charge: electrocorundum normal 63H – 2,5 kg; BG-3 – 0,14 kg; pulverbakelite SPF – 12A – 0,35 kg; magnesium sulfate  $\text{MgSO}_4$  dehydrated – 0,16 kg; graphite silver GS1 – 0,12 kg. Polycondensation is 2 hours. The testing results (9 products): solidity ST3,  $K = 6,76$  (stick with the diameter of 25 mm, the duration of sinking – 5 – 6 seconds).

### Example 4

Grinding wheels.

In addition to the other various authors’ experiments on their production, the grinding wheels (with the enlarged sizes) were also obtained as the results of an independent assessment at “Dmitrovgradchemmach” manufacture. The wheel of the typical sizes 1-150x20x32 (15 products) and 1-250x25x76 (8 products) were obtained using the formula of Example 2. Polycondensation (after heating to the temperature regime) - for 2.5 hours, followed by natural cooling oven. The products meet the necessary standards of the analogous products. The Test Report was made (see the Appendix). The product solidity is SM2 and S1, as it was planned. The surface and chips texture quality, successful break testing (SIP-800) and other are the evidence of high standards of these samples.

This paper is the primary publication, the principal aim of which is only a statement of the of the methodology’s approach to the problem. Therefore, the scope of the publication does not allow to present a large number of experimental results, sometimes very interesting, in the author’s point of view. All this he suggests elaborate in a separate monograph, preparing for publication.

### Conclusion

As a result of careful consideration of the wide range of literature and many special experiments it can be concluded:

1. The method of speeding up of polycondensation of thermoreactive composites on phenolformaldehyde bond was introduced and experimentally proved. This method consists of introduction of the dehydrated compounds like crystal hydrates able to form solid material into the charge as a filling. This allows transferring the main process from kinetic to the

diffusive – changing the concentration diffusion of the by-products removal in to the reactive diffusion. Various technologies of obtaining the PCM and products of different application reducing the energy consumption and increasing the productivity can be worked out based on this method. This process can be speeded up using the microwave heating [37]. It is confirmed with the results of the preliminary author's experiments.

2. We get an additional means of process control in the manufacture of thermoreactive polycondensation PCM. In particular, method can significantly increase the degree of polycondensation, its controllability at different stages. Moreover, given the "accentuated" by the exothermicity of the process as a whole, it is possible in the future to develop a process which consumes almost no external energy- using the scheme of chain chemical reaction.

3. The beginning of the creation of absolutely new materials – PCM with a kind of "double" matrix: like polymer and ceramic (inorganic nature) – were initiated Combined matrix can provide a significant improvement of the product.

Only the first step was made but the author is sure that the described process has a great future. It's fair to say that the idea to combine (in a kind of chemical compounds) volatile products - resulting in "swelling" (sometimes explosively) preprets when rapidly heated, - appeared in author's mind

while thinking of primary A. Nobel's ideas. It was him who applied it changing the highly explosive nitroglycerine into the dynamite with its chemical adsorption by the so-called "active" (adsorptive) fillings [38]. We used this idea in exactly the same way. That's why the author suggests to call this method as the "Nikitin's – Nobel's Method" (The Nikitin & Nobel Method) and the new type of materials (with the double matrix) – "ninobites" taking the first letters of the scientists' names and consonant to "dynamite". Alfred Nobel's wrongly forgotten ideas will vivify in development and effective application.

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