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RESEARCH OF MODIFIED ROSIN USABILITY IN MODEL COMPOSITIONS FOR PRECISION MOLDING

The research result of the modified rosin as a component of model compositions for precision casting is given in the article. The last five years successes in producing the latest products from rosin are reached. New rosin products essentially differ from rosin by physical and chemical properties possess certain advantages enable to expand the sphere of introduction and level rosin shortcomings. Therefore development and research of new model compositions for precision casting taking into account the achievements in the field of secondary rosin product synthesis is an actual task and promotes decelerating elimination in this area from foreign analogues.

The article shows depending on applied raw materials and conditions of physics-mechanical and operational properties. Possibility of production of the modified rosin products at the chemical companies of Belarus opens wide perspectives for development and manufacturing of new model compositions.

Introduction. The joint development strategy of petrochemical and oil refining industries (the perspective development program of the concern “Belneftehim”, Minsk, 2010) demands new composite structures development with use of polymer-, petro- and timber-chemical products.

The casting method by investment patterns due to its advantage in comparison with other ways of mold manufacturing has got a considerable application in mechanical and instrument engineering. The method allows to approach as much as possible molding to a ready detail, and in some cases to obtain the cast detail which additional processing before assemblage is not required. Thereof labor input, cost of products manufacturing sharply decreases, the metal and tool expense reduces resources are saved.

An indisputable fact for industrial model compositions (MC) manufacturing and development of new competitive MC with the improved operational properties is the following: precision casting will be always demanded by mechanical engineering. Now in the market of the CIS countries there are highly effective MC, presented by the firms “Kind Collins”(USA) and “Paracast” (Germany). The model compositions presented by Russia are made by JSC “Promarmatura” (Novocherkassk), JSC PKF “AIR Company (Nizhni Novgorod), FRGP “Salute” (Moscow), JSC “Echohim” (Shebekino) and etc.

The only one MC maker in the Republic of Belarus is Joint Stock Company “Factory of mountain wax” (bor. Svisloch). Its model compositions of brand ZGV-101, ZGV-102 and ZGV-103 (delivered on machine-building enterprises of the Russian Federation) are applied to obtain foundry goods of complex configuration from any casting alloys without machining or with the minimum operational development that considerably reduces the manufacturing cost of the parts at the expense of the metal shaving economy, and the volume reduction of mechanical work. However by the physics-mechanical properties domestic and made in Russia MC concede to the similar foreign analogues. Therefore, because of high value of mechanical engineering parts made by the technology of precision casting, the largest Russian engine-building enterprises accepted the decision to buy expensive structures from the far abroad of “Kind Collins” (USA) and “Paracast” (Germany) manufacturing. Thus, the manufacture of MC for Belarus is focused on export.

Depending on the kind of casting there are different requirements to MC: minimal ash content; homogeneous structure; possibility of reusing; minimal interaction with a fire-resistant cover; less than 1000 kg/m^3 structure density; minimal duration of MC hardening in a mold; a good fluidity of pasty MC; a good flowing of MC at mold melting; rather a low melting temperature (up 80°C); minimal shrinkage at cooling and heating expansion; guarantee of pure and glossy model surface; support a detail with necessary durability and hardness after removal from the mould in order to avoid deformation and damage during all technological operations.

There are more strict requirements for casting of turbine blades; for large-sized casting – the average requirements; for shaped casting – less rigid requirements.

Main part. For the purpose of working out innovative highly efficient MC we carried out the deep analysis of patent and scientific references on compounding, ways of preparation and possibilities of MC application in foundry manufacture for precision casting by investment patterns.

As carried out analysis has shown the most known model masses are those containing as components paraffin, stearin, brown coal wax and target additives [1].

The basic disadvantages of new paraffin-stearin models are a volume and linear shrinkage, a high factor of expansion on heating, a low durability and hardness. As a result, because thermal expansion of a model composition advances its fusion, cracks in the form occur; and one or some layers of fire-resistant cover are required for.

To decrease shrinkage and to increase the models durability a solid fine-dispersed filler – a carbon containing material that completely burns out on glowing of ceramic forms – is introduced [2].

However the specified model material is little economic, as does not assume reusing.

It is known a composition of model mass [3] that for decreasing shrinkage and increasing durability and time duration contains a high heat-conducting powdery metal at the following ratio of components, wt %: fusible organic component 25.0–60.0 (paraffin, stearin, brown coal or peat wax either their combination); a high heat-conducting powdery metal 40.0–75.0 (powdery aluminum of brand PAK-3 or PAK-4).

To decrease model composition shrinkage a model material is used in the mixed powder component forms of fraction 0.1–1.6 mm [4].

The products derived by hot mixture of wax and powdery filler are introduced for modeling, obtaining of molding forms and their using in any other areas. The given model structures fit for repeated application [5].

To raise geometrical and dimensional accuracy of models is possible at the expense of its manufacturing from powdery paraffin of fraction 0.1–1.6 mm. A cold sintering of composition is carried out at the expense of pressing. Porosity of models thus makes 3–10% [6].

We know a model composition [7] which up to 40–70% of air is introduced in. As a result, raising of dimensional and geometrical accuracy of models is succeeded at the expense of stabilization and shrinkage reduction of model mass up to 0,5–0,6% at expansion of introduced air, to decrease the expense of model mass on 30–50%, to lower pressure of press-fitting from 2–5 to 1 atm, to reduce the mass of large-sized models. Despite the occurrence of synthetic materials for melted model manufacturing natural waxes have the greatest application [8]. The model structure, of one of such compositions [9] contains, wt %: crude paraffin – 72.5; the refined beeswax – 15; crude mountain wax – 10; rosin – 2.5.

The application of wax models when casting by investment patterns is described in sources [10, 11, 12, 13, 14].

The wax model mass is used when casting by investment patterns for manufacturing of orthopedic implants with a textured surface [15].

It is known a waxy material compounding hydrocarbon with saturated chain and ratio of C : H content as 5.839 : 6.018 which is used for manufacturing of a model for a casting method by investment patterns [16].

The way of bracelets details casting by investment wax patterns [17], and the production of jewels with precious stones are known [18]. Wax models are also used at casting of trumpet connection [19] and other products [20, 21].

The composition [22] for manufacturing of investment patterns in which beeswax is replaced by a cheap microcrystalline wax (a product of oil refining, a mixture of paraffin, isoparaffin and naphthene hydrocarbons) is patented. The structure components, wt %, are: mountain wax – 50; microcrystalline wax – 30; ceresin wax – 10; rosin – 10.

It is possible to raise cleanliness of models and casts surface at the expense of structure composition application, wt %: paraffin – 20.0–30.0; polyethylene – 1.0–2.0; triethanolamine or dibutyl phthalate – 0.15–0.30; rosin – 35.0–39,0; ceresin wax – the rest. Uniformity of a composition thus improves saving its good strength properties [23].

There is a structure of model mass [24], containing dispergator, ceramic powder, a fraction in diameter less than 500 nanometers (nanofraction) in number of 2–74% from the volume of all mix, a fraction in diameter more than 500 nanometers (microfraction) in number of 3–74% from the volume of all mix, a metal powder, made of metals and/or an alloy, and/or intrametallic compounds, one or some additives, organic or inorganic binding.

We know a paraffin composition [25] for casting by investment patterns, containing as a filler polyethylene terephthalate in amount of 5–50% from the mass of a composite material. Polyethylene terephthalate reduces the composition factor of temperature expansion that promotes increasing accuracy of the casting sizes. Polyethylene terephthalate does not react with cast materials, allows easily to delete a composition from the form, reduces the danger of shell mold cracking and at burning does not form a significant amount of pitch.

For increasing durability of models and reducing shrinkage of a filler the modal composition [26] contains a powder of graphite and in addition rosin and ceresin at the following components ratio, wt %: brown coal wax – 27–40; ceresin – 10–16; rosin – 30–40; graphite – the rest.

The composite containing non-saturated hydrocarbons in which the content ratio of hydrocarbon and hydrogen constitutes 5.830 : 9.018, and the general content of carbon and hydrogen in hydrocarbon makes 98.5–100.0% are used for repeated application when producing investment patterns of difficult volume forms [27] on obtaining precision art casting.

On making turbines blades with internal cooling the casts are obtained by casting by investment patterns with premium quality surface. For this purpose the spherical particles of a defined material are used as investment pattern filler [28]. Thus the casting manufacture cost decreases, the surface quality improves, the percentage of cast cores destruction decreases. The size of particles is from 10 to 70 microns. Spherical particles demand making a smaller effort to fill a cast cavity.

The model structure [29] containing, wt %: ceresin – 15.0–29.0; polyethylene wax – 15.0–20.0; a copolymer of ethylene with vinyl-acetate (5–12 wt %) – 1.0–5.0; water – 2.0; paraffin – the rest enables to produce premium models (high accuracy of sizes, cleanliness of a surface, stable geometry) with the subsequent obtaining difficult thin-walled models with a glossy surface and exact geometry. Joint connection of polymer and water at a given ratio of model structure components enables to produce premium models.

It is known a model structure [30] on the basis of paraffin and in addition containing polyethylene and rosin at the following ratio of components, wt %: paraffin – 55.5–56.5; brown coal wax – 20.0–22.0; oil bitumen – 6.0–7.0; polyethylene – 3.5–4.5; rosin – 10.0–13.0. To reduce "tightening" polyethylene wax PW-300 can be additionally introduced into a model structure in the amount of 5–7 wt %.

We know a model composition [31] for investment patterns on the basis of paraffin, brown coal wax, oil bitumen, triethanolamine and in addition that one containing polyethylene, polyethylene wax and rosin at the following ratio of components, wt %: paraffin – 44.0–46.0; brown coal wax – 17.0–18.0; bitumen oil – 5.0–6.0; triethanolamine – 3,0–4,0; polyethylene – 3.0–4.0; polyethylene wax – 13,0–16,0; rosin – 10.0–11.0.

The model compositions [32] on the basis of paraffin and brown coal wax, extra containing polypropylene, asphalt butane deasphalting, and rosin at the following ratio of components, wt %: paraffin – 45.0–47.0; brown coal wax – 21.0–22.0; polypropylene – 0.8–1.5; asphalt butane deasphalting – 12.0–13.0; rosin – 17.5–20.2 are used for blades manufacturing of gas-turbine installations by investment patterns.

The model composition for investment pattern [33], containing a waxy model mass as plasticator, technical urea as filler, nonionic surface-active substance as emulsifier, potassium nitrate is known at the following component ratio, wt %: waxy model mass – 10.0–85.0; technical urea – 9.0–70.0; nonionic surface-active substance – 5.0–10.0; potassium nitrate – 1.0–10.0. Use of the given model mass allows to lower power inputs, to increase strength of model, to reduce defective goods.

The following compounding, wt %: ceresin – 18; polyethylene – 1.6; oil bitumen – 0.3; rosin – the rest is used for production of premium delicate models by thickness less than 1 mm and for reduction of composite cost price [34].

The composition [35] containing, wt %: synthetic ceresin – 11; brown coal wax – 6; fine-grain urea – 48; paraffin – 30.5; rosin – 4.5, as well as a composition [36] containing, wt %: paraffin – 58; brown coal wax – 30; polyethylene – 2; rosin – 10 are developed to improve wettability of refractory suspension, to increase heat-resistance and durability, and also to reduce linear expansion. However the last composition at the raised temperature indoors has insufficient durability and the raised shrinkage percent.

To eliminate the above-stated defects instead of polyethylene, polyethylene wax is used. Thus the ratio of components in the composition [37] makes, wt %: paraffin (basis) – 60 ± 2.5; brown coal wax – 10 ± 1; polyethylene wax – 20 ± 1; rosin – 10 ± 1.

According to the invention [38], the following compounding, wt %: oil paraffin – 45.0–55.0; brown coal wax – 35.0–45.0; rosin – 10.0–15.0 has been patented to increase bending resistance and reduce of linear deposition.

The model composite [39], containing, wt %, is: castor wax – 30.0–60.0; paraffin – 10.0–20.0; wax from rice bran – 5.0–20.0; polybutane – 2.0–10.0; rosin – 5.0–20.0; as well as the structure [40] containing, wt %: ceresin – 20–22; mountain wax – 10–12; paraffin – 38–40; stearin – 28–30 is known.

A model composition [41] on the basis of brown coal wax, containing, wt %: brown coal wax – 45–55, ceresin – 10–40, crystal wax – 15–45, stearin – 5, crude paraffin – 15 has got a wide application.

For casting of gas turbine plants blades the model composition [42] which contains paraffin, brown coal wax and polyvinyl butyl ether in amount of 1.0–20.0% of a total composite mass is introduced. The given composition provides production complex thin-walled models of high precision with raised durability and crack resistance.

It is known a composition [43] for investment patterns manufacturing of gas turbine plants. The composition contains a solid hydrocarbon and/or wax in amount of 0.1–70.0 wt %, and/or a copolymer with fusion temperature up to 300°C in amount of 0.05–20.0 wt %, as well as petropolymeric pitch in amount of 100,0%. A low temperature of pitch dropping and, consequently, a high fluidity allows to obtain casting models with the raised geometrical accuracy and hardness.

The composition [44] for casting by investment patterns of gas turbine plant blades and other casting details is introduced. The composition contains solid hydrocarbon and/or wax in amount 0.1–80.0 wt %, and/or polymer with fusion temperature up to 300°C in amount of 0.05–30.0 wt %, and also thermopolymer pitch in amount up to 100.0 wt %. Introduction of thermopolymer pitch enables to raise durability of a composite for the wide range of casting models with the raised geometrical accuracy.

Powdery paraffin pressing without preliminary cast heating is carried out to obtain the model of porosity 1.5–3.0% [45]. The model material thus conglomerates practically without phase of deformation with formation of open capillary porosity that compensates expansion of model melted from a ceramic cover in the course of its heating. Thus the raised dimensional and geometrical accuracy of models and casts is provided.

To raise the quality of models is possible by introduction of brown coal wax, bitumen BNK 45/90, rosin, high pressure polyethylene, brown coal wax PV-300 additional amount of polyethylene wax and triethanolamine at the following components ratio, wt %: paraffin of marks P1, V2, V3, V4 – 44.0–46.0; brown coal wax – 17.0–18.0; bitumen oil BNK 45/90 – 5.0–6.0; high pressure polyethylene – 3.0–4.0; polyethylene wax PV-300 – 13.0–16.0; triethanolamine – 3.0–4.0; rosin – 10.0–11.0 in a model structure [46] on the basis of paraffin. The obtained model structure V-1, VIAM-102 correspond declared compounding on linear shrinkage dimensions and heat resistance, but concede to them on crack resistance, to weight reflexivity, to the presence of "tightening", and also enable to use available compression molds for model manufacturing.

The following model compositions of brand MAI-9SH [47] and MAI-2SH [48], containing in great amounts rosin, that considerably improves thermoreactive properties, and also models shape stability. The composite MAI-9SH, wt %: paraffin – 9–20; polyethylene – 1.0–4.0; ceresin – 0.8–4.0; bitumen – 0.2–1.0; rosin – 73–89; and composite MAI-2SH contains, wt %: ceresin – 3.0–20.0; polyethylene – 1.0–2.5; bitumen – 1.0–4.0; a pitch – to 10.0; rosin – 77.0–89.0.

To raise the quality of models, foundry goods, ecological compatibility of process of making of the smelted models is possible at the expense of solid filler away from the model composite (carbamide); and to reduce a linear shrinkage size of a model composite – at the expense of brown coal wax and rosin, in addition polypropylene and asphalt butane deasphalting introduction in it, at the following ratio of components, wt %: paraffin – 45.0–47.0; polypropylene – 0.8–1.5; asphalt (ABD) – 12.0–13.0; brown coal wax – 21.0–22.0; rosin – 17.5–20.0 [49]. Besides, for increasing models rigidity polyethylene wax can additionally be introduced into the given model composites in amount 5.0 wt %.

A new composite [50] surpasses it in crack resistance, mass reflexivity, ecology, does not react with a ceramic cover and enables to use available compression casts for manufacturing by investment patterns.

On Fig. 1 it is presented a graphic generalized group compounding MC including a full set of necessary components, which in the fused condition are in homogeneous emulsified state.

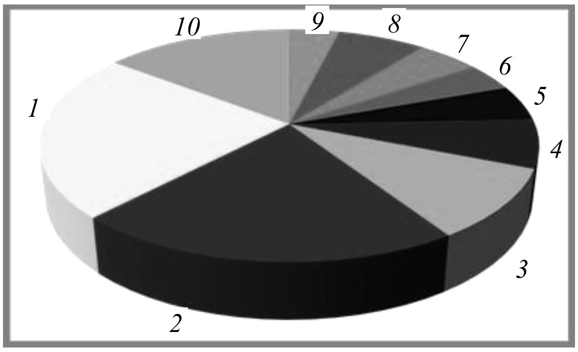

Fig. 1. Graphic drawing
of generalised group compounding MC:
1 – paraffin; *2* – brown coal wax; *3* – ceresin;
4 – polyethylene wax; *5* – peat wax;
6 – polymer additives; *7* – boric acid;
8 – ethyl cellulose; *9* – carbamide; *10* – rosin

Apparently from the data fig. 1, the most known model compositions contain components: paraffin, brown coal wax, ceresin, ethyl cellulose, peat wax, polystyrene, carbamide, boric acid, rosin.

Paraffin gives to models plasticity and stability to cracks formation. It is the cheapest and not scarce component of a model structure. Brown coal wax possesses a high durability and hardness, a considerable fragility, promotes a hard brilliant surface of a model. Ceresin possesses a higher plasticity and heat endurance, than paraffin. Ceresin is well alloyed with paraffin and stearin at temperature 70–80°C, with brown coal wax – at 100–110°C, with rosin – at 140°C. Ethyl cellulose – a variety of cellulose alcohol ethers, a fine-crystalline white or light yellow powder, is applied as plasticizer and reinforcer of paraffin and stearin composites, as well as the composites with rosin and ceresin. Peat wax possesses a higher durability and heat endurance. Shortcomings of peat wax are fragility, the raised viscosity in the fused condition.

Polyethylene increases thermal stability and durability of a model structure, is well alloyed with stearin and rosin. Polystyrene – the thermoplastic material used not only as an independent material for models manufacturing, but also as a component of a model structure, raising its heat endurance and mechanical durability. Carbamide – $CO(NH_2)_2$ – technical urea, at heating does not pass a softening stage. It provides a small linear shrinkage and high durability of a model. Boric acid provides a small linear shrinkage and high durability of a model. Rosin consists basically of pitch acids. It is a fragile glassy mass. It is applied for giving to model structures a higher durability and thermal stability. With a big content of rosin in a model structure it acquires fragility, sticks to equipment, loses technological reusing properties.

Nowadays on Joint Stock Company «Mountain Wax Factory», in MC compoundings except traditionally used paraffin, ceresin, brown coal wax, oleoresin is applied. Model structures of rosin contain, wt %: ZGV-101 – 10; ZGV-102 – 5; ZGV-103 – 10; V5K – 5 [51].

Pitch acids present in rosin (abietic, levopimaric,palustric, neoabietic, dehydrabietic, pimaric, isopimaric) give it unique properties: water stability; high film-forming properties; solubility in many organic solvents; a good combination with many polymer materials; plasticity; relative adhesion.

However rosin shortcomings are: crystallization in solutions, in polymer composites, in impregnating compositions and oils as a consequence of a big abiotic acid content in rosin; not rather high thermal-oxidative destruction, heat stability, thermal stability to oxidation by atmospheric oxygen in polymer composites. Because pine oleoresin is a seasonal product (it is extracted in spring, in summer and in autumn, as well as in various geographical places (Belarus, Russia, China, Brazil)) rosin obtained from it possesses various chemical composition and various physical and chemical properties.

One of the ways raising operational properties of MC and making them steady is using of modified rosin in composites. So, carried out earlier researches on using modified rosin (MR) – disproportionation rosin – in MC, showed that disproportionation rosin improves operational MC properties.

The works carried out by us (1990–2005 by EE BSTU, IPOC of Belarus NAS, CTC of Belarus NAS, ICNM of Belarus NAS) have shown that depending on depth of chemical rosin modifying by organic reagents (disproportionation, rosin polymerization, condensing by paraform, by diene acids, ethers, amides, imides on their basis) it is possible to obtain the products possessing a high plasticity, thermal-oxidative destruction stability, a high viscosity, softening temperature, high film-forming properties, lack of tendency to crystallization, in many cases a low acid number (AN = = 160–170 mg KOH/g, MR = 5–6 mg KOH/g). MR favourably differs from rosin by its physical and chemical properties, and the temperature interval is necessary for its producing (depending on updating) 140–270°C.

For the first time to obtain MC (Table 1) disproportionation rosin with T_S = 65.0°C and AN = = 163,0 mg KON/g, modified by triethanolamine.

Table 1

Composition and physical and chemical characteristics of disproportionated rosin

The sample	The duration-of disproportionation, h	Composition of pitch acids		Property of product		T_D^{DTG}, °C	T_D^{DTA}, °C	T_D^{av}, °C	E_D, kJ·mol^{-1}
		Acids with conjugated double bonds	de-, di- and tetra-hydroabietic acids mix	T_s, °C	AN, mg KOH/g				
PPR	–	77.6	7.0	72.0	172.0	230.0	210.0	220.0	70.0
$DPR_{0,5}$	0.5	40.0	44.8	69.0	168.0	245.0	260.0	252.5	80.0
DPR_1	1	5.0	80.0	67.0	165.0	263.0	275.0	269.0	91.0
DPR_2	2	3.0	81.1	65.0	163.0	272.0	290.0	281.0	100.0
DPR_3	3	2.8	81.9	62.0	159.0	264.0	280.0	272.0	96.0
DPR_4	4	2.4	82.0	60.0	156.0	262.0	278.0	270.0	91.0

Notes: PPR – pine pitch rosin;

$DPR_{0,5}$, DPR_1, DPR_2, DPR_3, DPR_4 – disproportionated pitch rosin obtained at presence of iodine catalyst (0.5–1.0 wt %) at $T = (220 \pm 5)$°C during 0.5; 1; 2; 3 and 4 h according to its subsequent pumping out at P = 20–30 mm hg;

T_s – temperature of a softening of samples (°C);

AN – acid number, mg KOH/g;

T_D^{DTG} – temperature of the beginning of a deviation of a curve differential; thermogravimetry;

T_D^{DTA} – the temperature has begun exoteric effect on curve DTA, the oxidation connected with the beginning;

$T_D^{av} = (T_D^{DTG} + T_D^{DTA}) / 2$ – temperature of destruction under the average data of curves DTG and DTA;

E_D – energy of activation thermooxidizing destruction.

The final product of modification according to GOST 12.1.007, by influence degree on an organism refers to the 4-th class of danger – to low-hazard substances that makes possible its using in compounds of model structures for precision casting. Physical and chemical properties obtained samples of the disproportionated resin and its salts were defined by a technique [52].

Dynamic thermogravimetry methods were used to determine thermal-oxidative destruction dimensions of disproportionated rosin and its triethanolamine salts [53].

The research is carried out by a derivative graphical system of the firm MOM type OD-103 in a sample heating programmed mode. The sample mas 0,1 g was warmed up in platinum crucible on air with speed of 5°C/minute. The Scale index − 100 mg, the galvanometer DTA − 1/3, galvanometer DTG − 1/10.

Apparently from given tab. 1, with time increase of rosin disproportionation − a maximum decrease in it of pitch acids content with conjugated double bonds (up to 2.4–3.0%) and increase of thermostable de-, di- and tetrahydroabietic acids (up to 81.1–82.0%) (reaction time duration 2–4 h, temperature (220 ± 5)°C, iodine catalyst 0.5–1.0 wt %) is observed. The most thermostable sample is disproportionated rosin DPR_2 (T_d^{av} = = 281.0°C).

This fact explains that the process of pitch acids decarboxylation which reduces the temperature of softening T_S and increases thermal-oxidative degradation stability T_d^{av} of investigated disproportionated rosin samples is observed with depth increase of disproportionation (reaction duration is more than 2 hours).

Further disproportionated rosin, for example DGR_2, after its obtaining at cooling in the reactor in the range of temperatures of 100−140°C mix with triethanolamine, stand at the set temperature 0,5−1,0 h aiming manufacturing of its triethanolamine salt with properties: AN = 2–4 mg KOH/g, T_s < 30°C.

Triethanolamine salt represents a light brown goop, soluble in organic solvents and water.

Then warmed up to fusion temperature ceresin, polyethylene and brown coal wax, paraffin is introduced and components are sustained before model structures formation (obtaining). A finished-product is poured out into cardboard forms where it finally solidifies.

Thermal stability dimensions of rosin triethanolamine salts according to dynamic thermogravimetry are represented in Table 2.

Apparently from given Table 2, use of disproportionated rosin salts considerably raises resistance to thermal-oxidative destruction T_D^{av} of obtained its triethanolamine salts. So, T_D^{av} for salt TASDPR (obtained on the basis of disproportionated pitch rosin DPR_2)is at an average on 45°C higher the similar T_D^{av} for TASPPR salt (obtained on the basis of pitch rosin).

Table 2

Dimensions of rosin triethanolamine salts according to dynamic thermogravimetry

The sample	T_D^{DTG}	T_D^{DTA}	T_D^{av}	E_D, kJ·mol^{-1}
	ºC			
PPR	230	210	220	70
TASPPR	314	310	312	90
DPR	272	290	281	100
TASDPR	324	389	357	120

On the basis of produced salt TASDPR with its various content (from 4,0 to 22,5 wt %) experimental MC which compounding is shown in Table 3 have been obtained.

Table 3

Model Structure Formula

Example	Experimental compound, wt %					
	Brown coal wax «Romonta»	Ceresin	Paraffin	Polyethylene wax PV-200	Disproportionated rosin	Triethanolamine
1	33.0	17.6	41.2	8.2	–	–
2	31.5	17.0	39.5	8.0	2.5	1.5
3	30.5	16.3	38.1	7.6	5.0	2.5
4	29.3	15.7	36.6	7.4	7.5	3.5
5	28.0	15.0	35.0	7.0	10.0	5.0
6	26.8	14.4	33.6	6.7	12.5	6.0
7	25.5	13.7	32.0	6.3	15.0	7.5
8*	35.0	20.0	30.0	2.0	10.0**	3.0

* The example 8 – a prototype [51].

** Unmodified rosin is used in the MC.

Besides, the component ratio (ex. 2−7): brown coal wax, ceresin, paraffin, polyethylene wax and DPR were calculated proportionally MC recipe, cited as an example (Table 3).

Determination of model compositions physical and mechanical properties: ultimate strength limit, heat stability, ashes mass part, dropping temperature and linear shrinkage – performed according to the method [54].

Physical and mechanical characteristics of obtained model structures are presented in Table 4.

Table 4
Physical and mechanical characteristics of obtained model structures

Example	Slow-bend durability at temperature (19 ± 1) °C, MPa	Heat stability, °C	Mass part of ashes, wt %	Dropping Point, °C	Linear shrinkage, %
1	9.5	44.0	0.14	99.0	1.2
2	9.0	48.0	0.12	97.0	1.1
3	8.8	52.0	0.10	93.0	1.0
4	8.5	54.0	0.07	92.0	0.9
5	8.0	56.0	0.05	91.0	0.8
6	6.5	57.0	0.05	89.0	0.9
7	6.0	58.0	0.05	87.0	0.8
8*	7.0	49.0	0.10	95.0	0.9

* The example 8 – a prototype.

It should be noted that model structures samples obtained on the basis of disproportionated tall rosin (are not presented in Table 4) possess the same physical and mechanical characteristics as the MC samples obtained with use of disproportionated pitch rosin.

The obtained research results were basic in compounding development and model structure ZGV-103M manufacturing technology.

Introduction of disproportionated rosin from 2.5 to 15.0 wt %, that corresponds to salt content TASDPR from 4.0 to 22.5 wt % (rosin salt wt % is determined by rosin and triethanolamine wt % total contents) into model structure formulae considerably improves compounding physical and mechanical characteristics (Table 4). Therefore, prototyping compounds correspond to the requirements by dimensions of linear shrinkage, dropping temperature, and mass part of ashes [54]. The more introduction of disproportionated rosin and then the more salt TASDPR content, the most considerable increasing of MC thermal stability (from 48.0 to 58.0°C). However, thus, decreasing of ultimate strength limit at slow bend of MC from 9.0 to 6.0 MPa is observed.

As we see from the data of the Table 3 and 4 the most optimal MC are these ones which compounding is given in examples 3 and 5. By their physical and mechanical characteristics (ultimate strength limit is 8.0–8.8 MPa and heat stability is 52.0–56.0°C) these MC considerably surpass a prototype [51].

Manufacturing scheme of model structure ZGV-103M producing process for precision casting is shown on Fig. 2. MC obtaining is exercised on installation (Fig. 2) that consists of the following equipment: reactor of stainless steel with heated shirt *1*, equipped with mixer *3* and motor reduction gear and charging door disposed on the cover with compactor, below the reactor is supplied with emptying fitting, overlapped by valve, heat generator *5*, filled by heat carrier (silicone oil) with adjusted heat generator, electric heating units, automatic sensor – temperature regulator and circulating pump *2* with electric drive; receptor of fiber drum for product unloading.

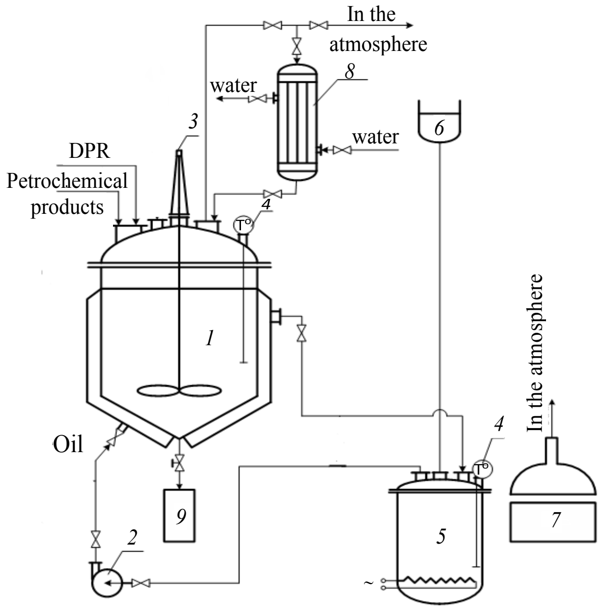

Fig. 2. Manufacturing scheme of MC producing for precision casting:
1 – the reactor with heated shirt;
2 – the circulating pump; 3 – the mixer;
4 – the thermometer; *5* – the heat generator;
6 – tank with heat carrier;
7 – the tank for rosin crushing;
8 – the refrigerator; *9* – the storage tank

Secondary equipment includes: scales, the thermometer for measurement of temperature in a reactor shirt (on Fig. 2 are not designated), two thermometers *4* for control of the heat-carrier temperature in heat generator and for measurement of a reactionary mix temperature, the metal storage tank *9* with a cover for possible melted reagents dumping, the tank for rosin crushing *7*.

Obtaining of ZGV-103M is carried out at the following components ratio: brown coal wax – 28.1 kg, ceresin – 15.1 kg, polyethylene wax – 7.03 kg, protoparaffin wax – 35.2 kg and triethanolamine – 5 kg, disproportionated pine pitch rosin – 10 kg. The set quantity of paraffin is loaded into the reactor, the heating is switched on, at temperature achievement of 80–85°C a mixer is operated and is mixed until obtaining a homogeneous mass.

Table 5

Physical and mechanical characteristics of industrial and developed model structures

Name of the sample	Heat stability					σ_t, MPa	E_e, MPa	ε_r,%	T_d, °C	MFI, g/10 min	a, kJ/cm^2	σ_b, MPa	σ_c, MPa	Sh, %
	$T_{5\%}$, °C	$T_{10\%}$, °C	$T_{20\%}$, °C	$T_{50\%}$, °C	E_D, kJ·mol^{-1}									
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
ZGV-101	252	277	309	339	87	2.6	550	1.1	85	0.20	3.7	4.5	4.0	0.9
ZGV-103	255	272	295	335	87	2.8	510	1.2	87	0.23	3.8	5.0	4.0	0.9
ZGV-103M	242	269	300	332	83	2.9	580	1.0	88	0.28	4.2	5.4	4.3	0.9

Notes. ZGV-101, ZGV-103 – the samples of the industrial model structures containing not modified PPR; ZGV-103M – the developed model structure containing DPR; E_D – energy of destruction activation; σ_t – tensile strength; E_e – the elasticity module; ε_r – relative elongation at rupture; T_d – temperature of dropping; MFI – a melt flow index; *a* – the specific impact strength; σ_b – bending stress; σ_c – compressive resistance; Sh – shrinkage.

Further brown coal wax and ceresin is loaded mixing into the reactor and the temperature of the reactor is raised up to 85–90°C. Polyethylene wax and disproportionated pine rosin is loaded into the reactor at temperature 90–100°C which are alloyed with the composite at temperature rising 105–115°C and constant hashing. Aiming acid number decrease and giving to the composite plasticizing properties triethanolamine reacting with disproportionated rosin in melt is loaded into the reactor at temperature 105–115°C.

Homogenization of model composition is carried out during 60 min. at temperature 105–115°C. In the course of reaction the temperature and the intensity of hashing is supervised. The control over a reaction course is carried out by sampling and definition of their dropping temperature and acid number. After obtaining a set dropping temperature and acid number by a reaction mixture a mixer of the reactor and the heating is switched off, the melt is cooled to temperature 70–80°C, the valve of emptying fitting is open and the finished product ZGV-103M is dumped in fiber drums through the filter with the size of a cell 0.16×0.16 mm.

MC prototypes obtained with use of disproportionated pitch rosin passed successful laboratory and broaden production tests at machinery enterprises of Russian Federation (Moscow) and were recommended for their producing at joint stock company «Factory of mountain wax» (Belarus, urban settlement Svisloch) with further using in foundry engineering for precision casting by consumable pattern [55].

Conclusion. Complex service properties analysis of designed model structure in comparison with industrial structures ZGV-101 and ZGV-103 (Table 5) has showed the following

1. By the characteristic «shrinkage» a new model structure does not concede industrial analogies. Shrinkage is caused by the phase transfer "the liquid – the solid body". Thus the more close molecules of model structures components approach to each other, the more is the shrinkage. Many chemical updates of one of the basic model structure components ZGV-101 and ZGV-103 – pine pitch rosin (PPR) – have not affected this important characteristic negatively. The value of the shrinkage dimension is in demanded limits: 1%.

2. The major model compositions characteristic – durability on a bend (σ_b) – was succeeded to be considerably improved. Chemically modifying PPR, it was possible to create compositions in which intermolecular system interactions are increased in three directions of their volume. As a result stability of a new model structure has essentially increased in force fields.

3. The major service property of model structures is their heat stability (in Celsius degrees) [54]. The new model structure substantially surpasses known structures by heat stability characteristic, and that may be explained by increasing of intermolecular interaction between system components.

4. The developed model structure with high characteristics "impact elasticity" and "static bending strength" at the expense of intermolecular interactions enhancement between the components constituent their structure, becomes less fragile, less rigid, more plastic. Therefore the model structure differs from basic structures, it is characterized by a higher value of tensile strength (σ_t TS, MPa), of compressive strength (σ_c, MPa) and relative elongation at rupture (ε_r, %) and smaller values of the elasticity elongation module (E_e, MPa). Thus, a composition which corresponds to the requirements on "shrinkage" characteristic, was succeeded to be created, it surpasses industrial analogues ZGV-101 and ZGV-103 in stability to all kinds of mechanical effects.

5. A melt flow index (MFI, g/10 min) is the major technological property characteristic of the plastics indicating liquid mass ability to fill forms, including difficult configuration.

6. The stability of a new model structure to aging provides its possibility to repeated use on a designated purpose.

As the conducted researches have shown, using the modified rosin in model compositions provides enhanced service properties of the latters. Presence of a sufficient raw-material base (a domestic renewed terpenoid raw materials) in the Republic of Belarus for rosin manufacture (Joint Stock company "Lesohimik"), and also possibility of its processing in by-products (Joint Stock Company "Lesokhimik" and Joint Stock Company "Factory of mountain wax") do potentially possible working out and output of new highly effective competitive compositions for precision casting.

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