Biopolymer bindings for casting manufacturing processes on the technological lignin basis

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Abstract. The paper analyzes the problem of using technological lignins to make new bindings for casting manufacturing processes. The reasons, restraining their application in casting manufacture, are considered. The objective (based on the physical nature of the material) and subjective (based on commercial benefit) reasons are presented. The paper considers the perspectives of application of technological lignins by the example of technological lignosulfonates use which is the main representative of the technological lignins family on the Russian market of bindings.

1. Introduction. State analysis

Technological lignin is the product of delignification of vegetable raw materials, which can be any vegetable tissues, from wood to seaweeds. This material is present in a vegetable cell invariably in different states, performing the function of binding which guarantees a general durability of the construction. That is why during processing it is generated as a by-product, as a rule, as a waste. The scale of the problem is so huge that in 1992 in Lausanne (Switzerland) the International Lignin Institute was established.

According to the Institute data [1], annually from 40 to 50 mln tons of technological lignin are generated around the world; the utilization of lignin is a matter of considerable difficulty and does not have a rational solution at present.

Russia, having the largest timber resources, is one of the main countries, generating technological lignin. Pulp-and-paper industry is the leader in this process. According to the estimations, presented in works [2, 3], the controlled volumes of annual generation of this product in its different forms (sulfite alkaline solution, technological lignosulfates, hydrolytic lignin, etc.) fluctuate in the limit of 4-5 mln tons. According to the data [4], in Russia about 95 mln tons of technological lignin have been generated for the recent period of the economical activity. According to the experts’ estimation, the volume of the vegetable raw materials processing will be increasing, it is expected that this index will have increased by 50-60% by 2050 [1, 4], in connection with this the problem of rational technological lignin utilization will be very acute both in the nearest perspective and in the future.

One of the most perspective areas of rational lignin use is application of its modifications as binding materials in casting manufacture.

The objective of the work was to estimate the possibilities of making binding materials meeting the modern requirements of casting manufacture on the basis of technological lignosulfates.
2. The course of doing the research

Technological lignosulfates (LST) are the modification of the technological lignin widely and traditionally presented on the Russian market of bindings. They are large-tonnage waste when processing timber into sulfite cellulose. This material was traditionally used in different productions, including foundry goods manufacture, as a binding material.

LST as a binding was widely-used in the USSR [5], for example in the work [6] it is pointed out that this material is the third in volume by being used in casting manufacture after clay and liquid glass. On the basis of the conducted researches, dedicated to the mixtures on the lignosulfonate basis, theses, including doctoral ones, were defended [7]. However, since the end of 90-ies the use of LST in casting manufacture has dramatically decreased, being substituted by various resin bindings. Nowadays this material is almost not used in modern casting technologies. The sphere of its use is limited to the production of simple castings, such as cast-iron moulds. The reasons for this are both of objective and subjective character.

Objectively, the binding on the LST basis do not meet the following modern requirements:

1) they do not have high strength properties, which are inherent in resin bindings;
2) they possess non-stable properties, this is manifested by abrupt (up to 30% of nominal values) fluctuations of material properties of different batches of the same manufacturer; and non-correspondence of the properties in case of buying material from another manufacturer; as well as the dependence of properties on seasonal temperature fluctuations;
3) they do not have enough thermal stability, being limited by temperatures 300-350°C;
4) casting rods and forms on their basis have high hygroscopicity;
5) the technologies of their use require thermal hardening, and this increases power inputs and prolongs the production cycle.

The subjective character of reasons for abrupt fall of lignin bindings’ use is that since the mid of 90-ies of the last century the casting sector of Russia has changed greatly, especially in the aspect of technological modernization. The equipment and technologies of leading western companies, prevailing now on the market, replaced domestic out-of-date technologies. It led to the replacement of domestic resource base of binding materials by imported bindings, as a rule, resin ones. On the one hand, the domestic materials were not adapted to work on the imported equipment (there was no interest in it); on the other hand, the market relations – commercial benefit, dictated the necessity of “tying” newly gained markets by foreign companies to their supplies. This was the reason, merely commercial one, for excluding domestic materials from the casting bindings market.

That time the chemical plant “Uralchimplast” was modernized, in practice it was rebuilt from the start, with the help of German investments of “Hüttenes-Albertus” [8], which is the leading manufacturer of chemical production for casting industry. Nowadays the enterprise is the leader in the production of casting binding materials in Russia; it is able to satisfy any requirements of the casting sector with modern resin bindings produced on the basis of the raw materials imported from Germany (!) [9]. A reasonable question arises, “What will happen if the supplies of raw materials from Germany stop?”.

The disadvantages of the lignin containing bindings have already been mentioned, but they possess a complex of positive properties which are withheld. They substantially excel the existing imported resin binding in these characteristics:

1) the source of the raw material for their production are domestic enterprises [3,7];
2) the cost of lignosulfonate bindings is incommensurably less: 4.5 – 6.0 rub/kg of liquid LST as against 3.5 – 5.0 euro/kg (265 – 378 rub/kg according to the present currency rate of ruble) for resin materials [2];
3) the technologies based on lignins are environmentally friendly: during transportation, during usage and during utilization [7,10,11];
4) the simplicity of storage: they do not require special regimes, have a long shelf life [7,10];
5) domestic casting enterprises have many years’ positive experience of their usage [7].
To understand the significance and perspectives of using lignin products for the time being it is reasonable to analyze the main tendencies in the development of casting bindings.

The bindings on the basis of technological lignin can be related to the biopolymer group of binding materials which are traditionally and especially actively developed in the countries of the European Union [12, 13]. The reason for the activity is connected with toughening of the requirements of sanitary and hygienic working conditions in the foundries and of the general ecological working safety of casting enterprises. This is presented in the materials regulating this area of their functioning [14] and reinforced in the Directive of 2010 year [15], which strictly regulates the application of resin materials on the phenol basis, which constitute 90-95% of modern casting bindings. This is connected with numerous researches having found out a negative influence of the mentioned above materials on the health of the factory personnel [16] and the population, living in the areas where the enterprises, using these materials, are located [17, 18].

The mentioned Directive [15] assumes a complete removal of similar resin binding materials from the production technological cycle. This conditioned the researches aimed at searching for the alternatives. In particular, compositions on the basis of different materials are offered: on the basis of protein materials [19], on the basis of starch [20], on the basis of different production wastes [21, 22]. Their common disadvantage is limitedness of the raw materials source in combination with high initial cost of separate initial components (starch); in connection with this the binding on the basis of technological lignin, in particular LST, could compensate these disadvantages.

3. Perspectives and possibilities

By its genesis lignin performs the function of binding separate elements of the vegetable tissue and provides leaktightness of the cytoderms, and due to its pigments it conditions the hue of the lignificated tissue. It is located in the nodes of intercellular space and in the cytoderms, providing a strong coupling of cellulose fibers. Such positioning leads to guaranteeing the strength – “lignification” of the vegetable tissue.

Lignin polymer is formed at the growing phase – plant’s lignification after the formation of the vegetable cell in the intercellular space and directly in the cytoderms of the cell itself [23].

The genesis of lignin explains the specificity of its structure and multi-factor of the influence on structure and chemical composition formation. This involves difficulties in the process of vegetable raw material technological processing, explains the impossibility of extracting natural lignin from the vegetable tissue in its natural state. That is why they distinguish between “protolignin” – the substance being directly in the plant and the material – the product generated as a result of the totality of technological influences for the delignification of the vegetable raw material.

It is necessary to point out that lignin is not purposefully produced according to rigid standards; lignin containing substances are obtained, as a rule, as large-tonnage wastes from different productions. In its turn this predetermines the indefiniteness of the chemical structure, multilayer structure and molecular-mass distribution of the generating lignin products. In the process of physico-chemical influences on the vegetable tissue, regulated by the specifics of the processing technology and the type of the initial vegetable raw material, the molecular mass of lignin is transformed; due to several times decrease its chemical activity undergo changes, the consistency and component chemical composition also change.

In chemical respect, lignin is not a single chemical substance; it is a composition of aromatic polymers of related structure. The true, empiric, or gross-formula of lignin can be presented as \( C_{288}H_{318}O_{102} \) [24]. A general view of the lignin material can be presented as a scheme – a structural formula (see figure 1). Its structural elements are phenyl-propane links, i.e. structural units which are derivatives of phenyl propane.

They distinguish technological forms of lignin materials, which can be found on the market, and thus being potential objects for further development: sulfate lignin, sulfite lignin and hydrolytic lignin. Exactly these materials can be the initial raw material for developing new competitive products for different needs. In this respect lignin containing materials are a typical representative of the functional
materials, a promising raw material for developing new binding materials for casting manufacture [25].

Figure 1. The structural formula of lignin [24].

The researches and results, obtained during preliminary approbation, allow claiming that the main difficulties can be overcome.

The problems of stability and strength properties’ improvement are solved by selecting modifiers [10,17,25], see figure 2 and figure 3.

Figure 2. The stability of binding property of LST compositions when testing during a calendar year: 1 – composition LST – NSAS, 2 – LST (without any processing).
Figure 3. The indicators of the effect of different classes’ substances (acids, salts, bases) on the binding LST ability, curves: 1. – nonionic surface active substances (NSAS); 2. – hydrochloric acid; 3.- sulfuric acid; 4. - nitric acid; 5.- sulfonic acid; 6- ammonium sulfate (12% water solution); 7- solution of caustic potassium; 8 – solution of caustic sodium.

The duration of hardening cycle can be considerably reduced due to the usage of blowing technologies, in particular, hardening of the rod, formed in a core box, with further blowing by hot air (see figure 4) and extraction of the finished rod. During 50 sec the necessary strength is obtained.

Figure 4. The possibilities of guaranteeing strength of binding compositions on the LST basis by different hardening methods.

4. Conclusions
The presented results of casting binding material development on the basis of technological lignin (LST) allows claiming the technological facilities of making binding materials on the basis of lignin materials which are capable to compete successfully with widely-used now synthetic resins on the phenol basis. Lignosulfonate materials can be considered as a typical example of resource-saving technology and rational use of the secondary raw material, generated from the renewable natural resource.
References

[1] Information database of International Lignin Institute(The electronic resource): http://www.ili-lignin.com/aboutlignin.php

[2] The survey of lignosulfates market in Russia 2015 (The information resource): http://www.infomine.ru/research/36/500

[3] Varfolomeev A A 2009 The development of environmentally friendly phenol-formaldehyde resins, modified by technological lignins The thesis for obtaining the PhD degree in Chemistry: qualification 05.21.03 “Technology and equipment of chemical processing of tree biomass; chemistry of timber” (Bratsk, Russia) p 160

[4] The government report of the state and about the protection of the environment of Irkutsk region in 2003 (Irkutsk, Russia: Oblmachinform) p 296

[5] Illarionov IE and Vasín Yu P 1992 Moulding materials and mixtures: monography (Cheboksary, Russia: The publishing house of Chuvash University) part 1, p 223

[6] Doroshenko S P, Avdokushin V P and Matisheik I 1990 Moulding materials and mixtures (Kiev, Ukraine: High School/ Prague: SNTL) p 415

[7] SemikAP 1987 Moulding and rod mixtures with binding materials on the basis of technological lignosulfonate The theses for obtaining the degree of Doctor of technical sciences: qualification 05.16.04 “Casting manufacture” (Kiev) p 225

[8] The information resource, the leading manufacturer of casting binding in Russia («Hüttenes-Albertus», Germany) access mode: http://www.huettenes-albertus.ru/

[9] Dibrov IA 2017 About conducting XIII International Congress of foundry workers and the international exhibition “ Casting – 2017” 19-21 September 2017 The foundry worker of Russia10 7-14 (Chelyabinsk)

[10] Rodionov O V and Yu O Svinoroev 2011 The formation of the environmental safety of region’s enterprises (Monographi, Lugans, Ukraine: “Knowledge”) p 232

[11] Suvorov B L, Goblina R I, Koravoev ES and et al 1987 Casting bindingsinthermassproduction: catalogue (Sverdlovsk) p 36

[12] Tackes I 2001 Core Binders: A Look into the Future Modern Casting 1024 –7

[13] Serghini A 2011 The future of organic foundry binders in Europe Przegląd Odlewnictwa 11-12, 548-53 (in Polish)

[14] European commission 2005 Integrated Pollution Prevention and Control Reference Document on Best Available Techniques in the Smitheries and Foundries Industry p 363

[15] The Directive of the European Parliament and Council of the 24-th November 2010 concerning industrial emissions 2010

[16] Löfstedt H, Westberg H, Seldén A I, Lundholm C and Svartengren M 2009 Respiratory symptoms and lung function in foundry workers exposed to low molecular weight isocyanates American Journal of Industrial Medicine 52 455-63

[17] Löfstedt H, Westberg H, Seldén A I, Rudblad S, Bryngelsson I L, Ngo Y and Svartengren M 2011 Nasal and ocular effects in foundry workers using the Hot Box method Journal of Occupational and Environmental Medicine 53 43-8

[18] Löfstedt H, Westberg H, Seldén A I, Bryngelsson I L and Svartengren M 2011 Respiratory symptoms and lung function in foundry workers using the Hot Box method – a 4-year follow-up Journal of Occupational and Environmental Medicine 53 1425-9

[19] Eastman J 2000 Protein – based binder update: Performance put to the Test Modern Casting 10 32-4

[20] Zhou X, Yang J and Guohiu Q 2007 Study on synthesis and properties of modified starch binder for foundry Journal of Materials Processing Technology 18 407-11, doi: 10.1016/j.jmatprot.2006.11.001

[21] Grabowska B 2009 Cross-linking of polyacrylan compositions with biopolymers with use of selected chemical and physical agents Polimery 54, 7-8, 19-20 (in Polish)

[22] Patterson M and Thiel J 2010 Developing Bio-Urethanes for No-Bake. Foundry Management
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