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IMPROVED SCHEME FOR INTEGRATED PROCESSING OFPINE RESIN *PINUS SILVESTRIS* L.

The review is devoted to the results of many years of work in the field of modification of terepenthene, rosin and turpentine. The article provides the advanced scheme of complex processing of the original materials. The last year's successes in producing the latest products from rosin are reached. The article shows depending on applied raw materials and conditions can produce composite structures with a wide range of physics-mechanical and operational properties.

Introduction. The genus *Pinus* is of the highest productivity of all the conifers of the family *Pinaceae.* The most common pine on the territory of CIS is *Pinus Silvestris* L.

In the second half of XIX century some businessmen of the forest industry proved the feasibility of pine resin harvesting in the forests of Belarus and Russia and the following rosin and turpentine production. To create and develop the rosin-turpentine production in Russia some efforts were taken and implemented by D. I. Mendeleev, F.M. Flavitsky and V.E. Tishchenko in the early twentieth century. The production of rosin and turpentine was created under the Academician V. V. Shkatelov in Borisov and Bobruisk (BSSR) in the 30s of the XX century.

Since wood is a renewable raw material, the sap obtained by tapping the pine *Pinus Silvestris* L., as a raw material is practically inexhaustible. Currently, the harvested pine resin is mainly used to produce rosin and partially its secondary products, which are used in many branches of the national economy. The resulting turpentine is often used as a solvent.

It was repeatedly attempted to replace rosin and its products with synthetic resins, but it has not practically led to significant results. In this regard, there is a steady upward trend in the national economy needs based on the rosin and turpentine of high quality.

Intensive development of various sectors of the economy of the Republic of Belarus and the increasing demand for the products of resin industries require elaboration of new highly efficient and practically important products based on the sap of the pine *Pinus Silvestris* L.

Main part. The traditional scheme of sap processing involves its removal of impurities, followed by separation by distillation into two groups of substances: monoterpene hydrocarbons - turpentine and non-volatile residue; rosin - diterpene acids and a mixture of neutral diterpenoids [1].

To produce rosin and turpentine of high quality pine sap is carefully cleaned of such ballast as litter and water as well as soluble substances and dyes which are rosin darkling substances. The rectification of purified sap (turpentine) is performed in such way that turpentine and resin were not presented in any boiling acid, and rosin did not possess any volatile components of sap. It was the problem of pine sap processing considering the ever-increasing quality requirements for finished products (rosin and turpentine) that many researchers tried to solve in the field of wood chemistry for two last centuries [2].

All methods of processing pine sap known today, aimed at obtaining rosin and turpentine, include: melting and dilution of sap with turpentine followed by turpentine distilling (turpentine production). They differ only in the sequence of operations, methods, materials and instruments design. At the same time, pine sap is a seasonal product harvested in spring, summer and autumn and in different geographical locations: Canada, Russia, China, and Brazil. As a consequence, rosin and its derived products have different composition with physicochemical characteristics which will subsequently affect the performance properties of composite structures (CS) derived from them.

There are many ways of complex processing of pine sap, bypassing the stage of its processing for rosin and turpentine (turpentine production).

Thus, many of the secondary products of rosin can be obtained from purified sap (turpentine). Very often it is quite justified because firstly it eliminates costs of turpentine production stage, and secondly, due to higher reactivity of pine sap acids some reaction occur at much lower temperatures than in the case of using rosin as a raw material. All of this results in production of finished products of higher quality such as rosin esters and dimers, hydrogenated rosin and turpentine, pimaric acid, rosin soap, etc. Diels– Alder reaction is especially worthy for these purposes. This method involves the use of turpentine coming from the decanter with the residual temperature of 100–140°C and having large number of levopimaric acid to react with maleic anhydride. The use of maleic anhydride allows you to receive various reinforced adhesives, maleopimaric acid, glycerol ethers of and maleinized turpentine, etc. However, as we can see from numerous papers [3], some researchers of the twentieth century just partially modified turpentine with maleic anhydride.

Therefore, the idea of the possibility of deep and explore turpentine modifying with maleic anhydride at the temperature range of 180–190°C is worthy being studied.

The heterogeneity of the chemical composition of turpentine (presence of resin acids of abietic type and of terpene hydrocarbons having system of conjugated double bonds), and the ability of the processes in the isomerization of resin acids and terpene hydrocarbons in the reaction give new prospects for wood chemical products production.

To enhance the possibility of using such efficient and unique natural product as pine sap, it is reasonably and practically important to carry out a wide range of studies to establish on the basis of resin acids and terpenes new efficient rosin substitutes – turpentine and maleic adducts with a wide range of physical and chemical properties. The elaborated substitutes cannot only be used for well-known composite structures, but also for newly developed ones.

Another important area of research is more detailed study of availabilities of production of modified resin and turpentine. It should be based on sap derivative. They should be synthesized using conventional methods of chemical modification and study their application in various compositions.

We made a lot of programs of state researches and budget contracts in the period of 1989–2014 years in the process of development of methods for the preparation of highly terpenoid secondary products based on the sap of Scots pine *Pinus Silvestris L.* with a set of useful properties. We tried to create on their basis highly effective and practically important compositions for various purposes. It allowed us to propose an improved scheme of sap complex processing (see the figure).

The improved scheme of complex processing of pinesap is supposed to involve some chemical modification of turpentine, rosin and turpentine oxygen, nitrogen and metal containing compounds. It helps providing a highly intensified production of the turpentine, maleic and rosin products, increasing the yields of target products, minimizing waste production, reducing the energy intensity of production and creating on their basis practically important compositions (Fig. 1).

Producing of turpentine and maleic addicts and composite structures based on them. The figure shows a flow diagram for production of RTMA or RTMR in the general scheme of processing of pine gum to obtain rosin and turpentine. It is obvious that the turpentine obtained by dissolving sap in reciprocal gum turpentine is used in all described industrial processes. If the stage of fractionation (boiling) of turpentine with the obtaining of turpentine and resin is excluded from the scheme, the use of methods [4, 5] becomes impossible because of the lack of the reciprocal turpentine. So producing of RTMR with methods [4, 5] is possible only if all technological scheme of the industry are in operation. In order to establish a RTMR production without breaking the technological process of turpentine processing to obtain rosin and turpentine, it is advisable to dissolve the co-again turpentine in the presence of extraction and sulfate turpentine [6].

Having been modified turpentine with maleic anhydride and styrene, we managed to get a new wood-chemical product RTSMR [7].

In order to reduce the temperature of RMA adduct we proposed method for its production in the presence of a catalyst NH_4I [8].

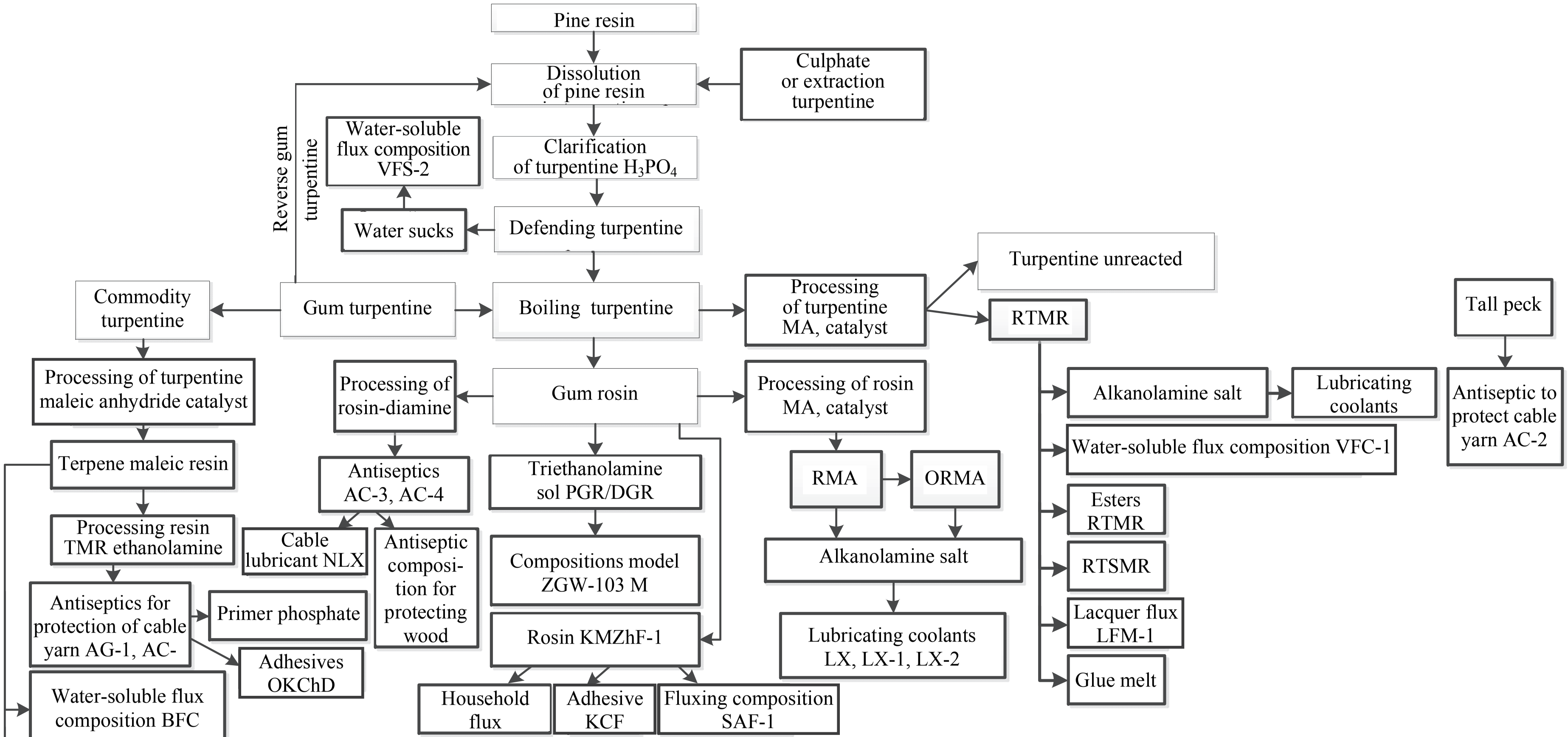
Turpentine processing in the presence of maleic anhydride in the presence of a catalysts P_2O_5, NH_4I, NH_4Cl [8, 9, 10] allowed us to derive TMR resins with a high yield.

In view of the fact that in the process of production of turpentine and maleic adducts unbound maleic anhydride may remain we developed the method of their stabilization by oleic acid [11].

The proposed technology of RTMR, RTSMR, TMR RMA and ORMA adducts production, in our opinion, may be of interest for both Belarusian and Russian manufacturers. The availability of raw materials (rosin and turpentine), simplicity of adducts production, their high reactivity properties (AN = 265–320 mg KOH/g) covert these resins into a valuable chemical raw materials for production of some new products and CS based on them.

Alkanolamine (ethanol-, diethanol- or triethanolamine) or sodium salts of RTMR can be used as a lubricants and surface-active materials in LX, LX-1 and LX-2 coolants compositions [12, 13] used in mechanical treatment of ferrous alloys. Ammonium salts RTMR due to their high chemical activity with copper oxides can be used in the process of production of water-soluble fluxing compound of BFC-1 to tin copper wire for mechanical works at T = 240–280°C instead of traditional fluxes [14].

The formula of protective fluxing coatings was developed on the basis of RTMA [15]. It is a fluxing lacquer LFM-1 to protect the pin elements of electronic components from oxidation during the soldering process and at the same time serving as a flux.



THE MAIN PRODUCTS OBTAINED IN THE COURSE OF THE STUDY

1. ADDUCTS	ORMA, OTMR, RTMR, RTSMR, TMR;
2. ANTICEPTICS	AC-1, AC-1M, AC-2, AC-3, AC-4;
3. VARNISHES	LA-6, LA-6G;
4. LUBRICATING COOLANTS	LX, LX-1, LX-2, LX-2M;
5. FLUXES	CAF-1, lacque-flux LFM-1, BFC, BCF-1, BCF-2, household flux;
6. MODEL COMPOSITION	ZGW-103M;
7. ADHESIVES	KCF, adhesive OKChD, Water-soluble adhesives.

Improved scheme for the complex processing of pine oleoresin of *Pinus Silvestris L*

The high thermal RTMA stability allows to use it to produce thermoplastic compositions, e.g. in hot melt adhesives [16] for gluing radio components. Due to the high thermostability of properties ethers on the basis of RTMA can find application in the compositions exposed to the temperature loading.

Due to the high thermal stability, lubricant properties and resistance to corrosion, alkanolamine and sodium salts of RMA and ORMA are used to produce a number of lubricating coolants LX, LX-1 and LX-2 [8, 11, 13, 17].

Due to the presence of the anhydride ring, TMR can be utilized to give TMA imides having antiseptic properties AC-1 и AC-1M. Antiseptics that superior the industrial antiseptic named NFM was developed to protect cable yarn from damaged caused by aerobic and anaerobia bacteria [18, 19]. It is also used as an adhesive in the adhesive [20] and anticorrosive [21] compositions. Compositions methods of insulating lacquer making LA-6 и LA-6G [22] was developed on the basis of TMR.

Alkanolamine TMR salts found their application in lubricating coolant LX-1 [8, 13] and a water-soluble fluxing BFC composition [23].

Obtaining secondary rosin products and composite compounds based on them. As you can see from the fig.1, in the process of rosin chemical modification by diamines (ethylene diamine, diethylene triamine, gexamethylene diamine) antiseptics (amides) AC-3 and AC-4 [24, 25] can be produced. Their biocide properties (resistance to mold fungi, wood-staining and wood-destroying fungi) are similar or exceed the properties of industrial antiseptic NFM. Impregnating compounds for protecting wood and rope yarn derived from them can be used in industry. Triethanolamine salts derived on the basis of industrial PGR and DGR are used in the formulation of model compositions for precision casting type ZGW-103M [26, 27] which are used by machine-building enterprises of Russia. DGR sodium salts can be used in adhesive compositions for gluing paper labels [28, 29, 30].

In the process of using glycerol for partial rosin modification, rosin of higher fluxing properties (KMGF-1) was produced and a fluxing composition of CAF-1 [31] for the protection of MCB and MCBM wires and cables and KCF adhesive for bonding ferrite cores were developed on its basis [32].

Production of composite compounds based on rosin-turpentine and pulp and paper production wastes. The household soldering flux [33] was developed on the basis of waste (rosin oil) produced in the process of rosin production (KMGF-1). The soluble soldering flux (BFC-2) [34] was produced on the bases of sludge-water of rosin turpentine production. This kind of water is produced by turpentine washing.

Table

Quantity of experimental, experimental-industrial and industrial batches

Product type	Quantity, T	Production plant
RTMR	10.0	PD “Orgkhim” (Nizhegorodsk region., Uren, Russia)
TMR	27.0	Ltd “Lesokhimick” (Minsk region., Borisov, Belarus)
AC-1	30.0	Ltd “Lesokhimick”(Minsk region., Borisov, Belarus)
TMR	1.0	PD “Orgkhim” (Nizhegorodsk region., Uren, Russia)
LA-6G	1.4	PD “Orgkhim” (Nizhegorodsk region., Uren, Russia)
BFS	1.5	PD “Orgkhim” (Nizhegorodsk region., Uren, Russia)
ORMA	3.0	Ltd “Mountain wax plant” (Minsk region, Svisloch, Belarus)
Lubricating coolants LX, LX-1, LX-2	360.0	Institute of chemistry of new materials of NAS of Belarus NAS (Minsk, Belarus)
AC-2	2.0	PD “Solombalsk PPM” (Arkhangelsk, Russia)
ZGB-103M	2.3	Ltd “Mountain wax plant” (Minsk region, Svisloch, Belarus)
TOTALLY:	438.2	

The figure shows that an antiseptic composition of AC-2 [35, 36] to protect the cable from damage yarn aerobic and anaerobic bacteria may be produced by the chemical modification of tall pitch (waste pulp).

Improved complex scheme of processing pine resin *Pinus Silvestris L.* is confirmed not only with patents and certificates of invention but also, by their production by various wood chemical enterprises. The table given below demonstrates the quantity of experimental, experimental-industrial and industrial batches at different times of 1989-2014 years.

A wide range of researches improved the well-known traditional scheme of complex processing of pine resin *Pinus Silvestris L*. The pass-by products designed and manufactured according to the diagram and CS based on them may be interesting for different Belarusian and Russian producers.

Conclusion. An improved scheme of complex processing of pine resin was developed. It involves deep chemical modification of turpentine, rosin and turpentine oxygen-, nitrogen- and metal-containing compounds, while providing the intensification of highly effective processed maleic anhydride terpenoid and rosin products, increase product yield, waste minimization, reduction energy intensity of production and creation on the basis of their practical importance CS. A wide range of pass-by products and CS based on them were implemented. They included adducts, antiseptics, thermosetting paints, coolant, fluxes, model compounds, adhesives and many other compounds which are of great importance for enterprises of the Republic of Belarus and the Russian Federation.

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