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ANTISEPTICS ON THE BASIS OF TERPENOID COMPOUNDS: SYNTHESIS, PROPERTIES AND APPLICATION

Currently, chemical methods of pest bio deterioration of materials, products and constructions are the main complex of destructive actions. In particular wood preservative very effective way to save forest resources for the longest time protects. In developed countries, the use of antiseptics reached industrial scale. The search of effective forms of applying antiseptics and rational use of them continue to be relevant tasks. The review is devoted to the methods of antiseptics on the basis of the terpenoid compounds. It is given broad spectrum biocide properties of antiseptics and use of anti-septic funds in protective compositions and coatings for various purposes.

Introduction. In practical activities natural materials based on cellulose are widely used: wood, paper, cotton, flax, hemp, etc. At the same time cellulose materials are a source of carbon food for many live organisms first of all for filamentous fungi.

The greatest damage to wood is caused by the wood destructive fungi of the *Serpula and Coniophora* sorts causing rough decay of wood and resulting in so-called dry-rot fungi. Fungi of brown decay utilize generally cellulose, leaving dark amorphous sites which from a touch are easily scattered in powder.

The lowest (mold) fungi have rather low wood destructive ability, but quickly destroy fibrous materials. They can influence outside opportunities of the highest fungi and are steadier against adverse factors and many antiseptics.

Among measures of fight against the bio damages of materials caused by filamentous fungi, the first place is won by chemical means of protection. The Antiseptic Structures (AS) have to meet a number of requirements: to be toxic in relation to fungi and insects, but harmless to the person and animals; it is good to get into material; to be resistant in time; not to reduce durability; not to spoil appearance; not to be washed away by water etc.

For bio protective processing water-soluble, soluble in organic solvents and oil antiseptics are used. After the fungicidal treatment of cellulose materials considerably increase their operation terms.

Despite of the rather wide choice of AS, the problem of protection of materials, products and constructions from biological damage still is actual as just the known losses from biodeterioratios are 5–7% of cost of a world industrial output and they tend to grow.

Fungicidally treated wood is a very effective way of economy of forest resources, providing the longest terms of protection of wood. In the developed countries application of anti-septic tanks reached industrial scales long ago.

Now traditional chlorine-containing bactericides (chloramine, hypochlorite, etc.), the copper naphthenate, preparations containing α-pyrene, and also phenolic preparations in which a number of essential shortcomings are inherent: high toxicity, rather low activity concerning the majority of pathogenic microorganisms and fungi are prevailing in Belarus. Besides, their working solutions are poorly stable, active to corrosion, have the expressed unpleasant smell, irritate skin and mucous membranes, damage the protected materials.

Antiseptics are bought for foreign currency at high price in Germany, France, Russia, China and other countries. Production of them in the Republic of Belarus has limited character (JSC “Lesohimik”).

Development of a wide range of highly effective terpene products on the basis of domestic timber-chemical renewable raw materials possessing antiseptic, adhesive and anticorrosive properties will promote import substitution, decrease in prime cost and increase of competitiveness.

For the analysis of qualitative structure of antiseptic tanks on the basis of products of timber-chemical production patent search in a wide time interval was carried out.

Formulations and ways of receiving anti-septic tanks on the basis of timber-chemical raw materials are given below.

Main part. The effective way of protecting wood, consisting in use of the means, containing as an active ingredient high-terpene natural oils, including pine oil in amount of 50–90% is developed [1].

Industrial wood fungicidal treatment implies its deep impregnation. To prevent biological damage and increase the durability of wood composition [2] containing synthetic oligopyrene rubber with a molecular weight of 15.000–25.000, bitumen of oil and turpentine is offered. Turpentine provides intensive and deep penetration into the capillaries of the wood. Significantly more efficient transportation of hydrophobic components (synthetic rubber and bitumen) into interfebrile and intercellular pores of the wood is carried out, it provides deep impregnation of wood, ensuring the most reliable and durable protection, eliminating the need for heat treatment of wood.

In the article [3] the benefits and environmental safety of application of natural compounds of plant origin with biocide activity (alkaloids, terpenes, essential oils, etc.), the current state and future prospects of their sources, bioactivity and mechanism of action is examined.

In the work [4] tests for the presence of fungicidal activity `of seventeen compounds of terpene nature produced. As the most active products β-terpenol and sulphate turpentine are identified. It is shown that the α-terpenol provided fungicidal effect on 14 species of micromycetes being active bio destructors of various industrial materials.

The method of application of an antiseptic [5], comprising a non-toxic treatment of wood with a composition comprising as an active ingredient, pine oil, with a high content of terpenes is known. The composition comprises a surfactant in an amount of 20–35%, pine oil 4–10%, 60–70% water.

The antiseptic composition with "knockdown"-effect which comprises a synergistic mixture of pine oil of eucalyptus oil [6] is developed.

Aqueous solutions [7] having bactericidal and fungicidal activity and low toxicity for the use as disinfectant, comprising (wt %): mono- or dialdehydes 1–20, quaternary ammonium compounds 3–35, ethoxylated fatty alcohols 1–15, insecticides 0.5–15, and the rest – terpenes (e. g., terpenol) and dyes are offered.

Antiseptic [8], comprising a carrier – shivyrtuin (montmorillonitezeolite tuff) and as active substances – the composition of the following compounds (wt %): terpinol 60.7–75.2, D linoleatsetat 8.0–12.0 essential oil Grindel absolute 3.8–6.5, diethyl 7.0–10.0, menthol 4.0–6.0, fir oil 1.8–2.3, lavender oil 0.2–2.5 is developed. This antiseptic is non-toxic when used does not cause irritant, convenient to use, as it is a compactly packed powder, granular or compressed mass impregnated with the composition, which plays the role of the active substance.

The structural-group composition of turpentine oil is set in the sources [9, 10]. A scheme of allocation of mono- or sesquiterpene hydrocarbons and terpene alcohols is developed. Dedicated terpenes have insecticidal, insect repellent, fungicidal activity.

Components of extractive substances of wood have high physiological activity and may be used in agriculture as fungicides and plant growth-stimulating preparations for plants.

In work [11] the new approaches to biologically active compounds using rosin-extraction polymers, and various terpene compounds used for suction, deodorization of space for processing of various plant seeds are presented. Their fungicidal activity is investigated.

Repellant [12] containing terpenes (hydrocarbons), terpenoids, particularly terpenes, terpene esters, unsaturated terpenes (pinene, limonene), terpenoids with aldehyde functional groups is known.

The method of obtaining a biocide "Efiran-128" [13] is known. As an active ingredient the reaction product of α-chloromethylcyclohexyl ester fraction with pinene wood turpentine in the presence of $ZnCl_2$ is used.

For impregnation of wood the melt [14], a mixture of natural resins (acid gum, terpene resin) and waxes is proposed to use. Natural resins are subjected to modification by esterification, dimerization, hydrogenation, disproportionation, akrillation and reactions of Diels – Adler, oligomerization or polymerization. The melt contains flame retardants, antistatic agents, antimicrobial agents and protective agents against UV radiation.

A method of allocating the amount of biologically active acids with fungicidal and growth-stimulating activity of chopped green fir tree is proposed [15], which comprises isolating the desired product by extraction with an organic solvent, such as ether, from shredded green fir tree, which is pretreated with an aqueous alkali solution with a concentration of 0.5–50%. Dedicated triterpene acids have fungicidal and growth-stimulating activity and can be used in agriculture to protect and increase productivity of plants.

The influence of triterpene acids (drug "SIL-KA") on the productivity of rice plants of types of Commander is investigated. The positive effect of triterpene acids on indicators of productivity, regardless of route of administration is established – there was an increase grain yield by 17–20% in comparison with untreated controls [16].

Environmentally friendly biotechnological composition for protection of forest plantations from pests based on pine oleoresin, performing the combined functions of the agent stickiness, structure and biological activity developed.

Ecologically clean biotech composition for protection of forest plantations from pests based on pine resin performing combined functions of stick-

iness agent, structuring and biological activity [17] is developed. Additionally, the composition contains the ester plasticizers added in an amount of from 20 to 40 wt %. In order to stabilize the properties of the composition antioxidant 2,6-di-tert-butyl-4-methylphenol or ionol in an amount of 0.01–0.10 wt % is added. The use of a given composition enhances the effectiveness of pest control forest plantations. Ease of application and good fixing ability on plant sites are combined in them with a high biocide effect.

In the work [18] the types of chemicals whose main purpose is to destroy and prevent the growth of microbes (biocides) and their effectiveness in the application for the intended purpose are considered. As discussed biocides biologically active acids extracted from ground wood and their effectiveness in ensuring the stability of aqueous systems are used.

Wood preservative [19] is designed; it contains wax (natural wax, paraffin wax), high molecular weight carboxylic acids, terpenes, antioxidants, and others. The conservant has T_m = 50–80°C, AN = 15–27 mg KOH/g, saponification number 50–80 mg KOH g. In particular, the preservative comprises 40% wax, 28% terpene fractions, 20% paraffin and 10% stearic acid.

Bactericidal cover [20], comprising (wt %): pyrethroid bactericide 0.1–2.5, acrylpimaric 5–10, attractant 0.01–0.1, propellant 30–60, solvent 30–50 is patented.

In reference [21] a new waste technology of deep complex processing of resin of coniferous trees is presented, it provides the production of new environmentally pure products which have no analogues abroad, particularly neutral oleoresin – larch neutral resin (RNL), fir neutral resin(RNF), as well as their terpenes and balsams [22].

Method for producing RNL, allowing a resin which chemical composition is close to the chemical composition of neutral hard boiling sesqui diterpenoids of larch turpentine is proposed. In addition, it becomes possible to obtain the desired product with predetermined properties and levels of quality meeting the increasing demands of various customers, primarily businesses perfume and cosmetics industry [23]. Neutral gum resin is a mixture of high neutral diterpenoids. In appearance RNL and RNF – a thick mass of inactive amber to light brown in color with the temperature of dropping 18–25°C. Mass fraction of water – no more than 0.2%; mass fraction of solids – not more than 0,02%; mass fraction of alcohol – within 40.0–65.0%. For RNF dropping point is 20–26°C. The acid number of the resins – less than 4 mg KOH/g. On the basis of RNF and salts triterpene acids new drugs of anti-inflammatory, antibacterial and fungicidal actions are developed.

Sticky mass for catching insects [24], which has fungicidal properties is patented, it comprises (wt %): rosin 56–66, ceresin 2.6–2.8, rubber1.3–1.4, triethylamine 1.1–1.2, canola oil 14.0–18.0, industrial oils – the rest.

A method for producing highly fungicidal compositions for wood protection is offered [25]. The method is based on the interaction of Cu $(OH)_2$ or a mixture of CuO with the resin and fatty acids or alcohols, terpene hydrocarbons at T = 120–160°C in the presence of AcOH or other carboxylic acids.

The impregnating composition for the manufacture of anticorrosive packaging paper [26], comprising the reaction product of tall oil with an alkali metal compound selected from the group consisting of Ca, Mg, Li, Zn, Cu, Cd or mixture thereof is known. The main advantage of the impregnating composition is the possibility of obtaining homogeneous non-stratified coroplasts of the known biocides with fatty compounds by the use of the impregnating composition tallates of metals selected from the offered row.

As a binder in the manufacture of bio stable super hard fiberboard the neutralized reaction product of tall oil with copper sulfate is used [27].

Fungicidal activity of resin and fatty acids significantly increases with the introduction of a molecule of ester groups and quaternary ammonium salts [28].

Preparations [29] containing, as the active component dehydroabietic acid tin salt, where R – alkyl or phenyl, substituents – halogen, alkyl, alkoxy are known.

In the article [30], studies on the preparation of wood conservants based on pine resin and carbonates are reflected.

Biocide product for protection of wood and metal is known [31]. Its members except biocide components include transparent varnish, lacquer based varnish resin and varnish oil. Clear lacquer contains nitrocellulose, dammar acid, esters of resin acids. The drug prevents rotting wood and metal corrosion.

In the work [32] issues of synthesis of biologically active substances on the basis of wood rosin acids are reflected. By introducing new fungicidal groups into molecules of resin acids bactericidal fungicidal compounds (esters, imides) are synthesized. It is shown that maleopimaric acid esters and their derivatives have the improved fungicidal activity.

Composition for the impregnation of wood [33] comprising the soluble portion (e.g., a mixture of copper oxide 5–15 wt % and rosin 85–95 wt %) and the organic solvent (e. g. turpentine) in the ratio 2 : 3 is known. The composition protects the timber against rot, fungal attack and insects.

Biocide formulations for wood protection [34] are developed. To protect the wood from degradation

and at the same time to improve its form compositions comprising (wt %): pine oil with the addition of abietic resin 5–50, pigments (Fe oxide or carbon black), compounds of the biocide action (pentachlorophenol) 1–10, oil solvent or mixture of solvents (white spirit, turpentine) 40–85are suggested.

Wood conservant and a method for manufacturing wood conservant [35], which contains vegetable oils derived from processing of crude tall oil such as rosin acids and fatty acids are received. Wood conservants according to the invention is produced from crude tall oil by removing it from the neutral components, preferably removing

the compound, acting as a nutrient medium for the supply and rot fungi Compounds that increase the degree of esterification, such as steroids, including sitosterin and / or fatty alcohols also are removed. Rot resistance tests and studies, carried out for the crude tall oil confirmed that by using a mixture of resin and fatty acids obtained from the crude tall oil the best effect of preventing decomposition of wood is yielded.

The composition for the treatment of wood with water-repellent and fungicidal properties is proposed [36]. For the production of the given composition a concentrate capable to be emulsified is used, it contains pentaerythrityl ester of rosin acids, fatty acids, polychlorophenols, paraffin, alkilalkanolamin, water immiscible solvent and water.

Insecticidal and fungicidal wax [37] suitable for wood products are prepared by melting the mixture with stirring, wt %: wax “cire E” 54 wax “cire S” 17.5, wax “cire OP” 47.5, carnauba wax 8,5, rosin 8.5, paraffin 51.5, “Emulphor O” 34.5, technical $C_6C_{15}OH$ 10.7.

A method of producing the fungicidal composition [38], by treatment of gum rosin melt at 150–180°C by tin compounds $R_3SnOSnR_3$ is known, where R – ethyl, butyl, phenyl, during its gradual introduction.

No aqueous stable composition [39] based on tall oil, containing as active ingredient and thiazolopyrimidines insecticidal and fungicidal activity is developed.

Liquid fungicidal composition is proposed [40], which allows to reduce the dose-of Cu-derivative, which is an associate of tallate Cu, prepared by reacting tall oil (mixture of 45–95% of fatty acids such as oleic acid, linoleic acid and 2–45% abietic acid), and Cu salts or hydroxide with one or more other organic fungicides (cymoxanil, fosfotthyl Al).

Trans-isomers which was prepared from trans-$RhCH = CHC_6H_3 (OMe)_2$-3,5, contained in a head fraction of tall oil and (CH_2) in the presence of an acid catalyst such as an acidic clay are used as biocide [41]. As trans- isomers they propose to use a compound of formula (2-PhCH = CH-CH-4,6-$R_2C_6H_2)_2CH_2$, where in R = MeO- or -OH.

For wood preservation they propose to use a mixture of pentachlorophenolate copper (approximately 3%) and the methyl esters of tall oil fatty acids [42].

A technology for the industrial production of waterproof antiseptic compositions [43] on the basis of bakelite and pitch varnishes, which are used in the drying of raw timber to prevent them from rotting, is developed. Wood tar pitch has a softening point 80–130°C. Wood resin content in pitch protectant formulation is 50–80%.

Antiseptic packaging material [44] for steel made of two layers of crepe paper impregnated with paraffin distillate or slack wax, bitumen and glued is proposed. The material contains crepe paper soaked in a mixture of paraffin or distillate slack with tall pitch, in the following ratio (wt %): crepe paper 20–45, bitumen 20–50, paraffin or slack distillate 20–40, tall pitch 1–5.

Industrial fungicide is proposed [45], it comprises, as an active ingredient a product maleopimaric acid, which has antimicrobial activity against bacteria, fungi, yeasts. The active ingredient can be administered in a variety of industrial products or intermediates for their preparation, in admixture with a suitable carrier or other fungicide.

In the work [46] derivatives of N-substituted imides of the maleopimaric acid, exhibit fungicidal activity, and their method of preparation are represented.

In the article [47] the method for producing and the properties of N-(hydroxymethyl)-imide of the maleopimaric acid having fungicidal activity is considered. Of the acid imide maleopimaric (T_m = 282°C) and CH_2O N-(oxymethyl)-imid of maleopimaric acid $C_{25}H_{35}$-NO_3 is obtained, yield 74.5%, T_m = 215°C.

A method of producing antiseptic composition AC-1 [48] obtained by treating terpenomaleic adduct (TMA) by ethanolamine at elevated temperatures is developed. The received product containing N-(hydroxyethyl)-imid TMA may be used instead of copper naphthenate (as fungicide) in the manufacture of formulations used to impregnate the yarn and wood pulp.

Conclusion. The analysis of published data and the range of products produced by wood chemical companies in Finland, USA, Germany, Canada, China and Russia shows that a wide range of antiseptics based on renewable wood chemical raw materials is developed, it has a spectrum of biocide properties, which can be used in protective coatings of various compositions and destination in the electrical, paint, wood, pulp and paper industry and mechanical engineering.

The most common conservants are derived from rosin, tall oil and turpentine.

High physical and chemical properties and the possibility of production of terpenoid products in the chemical industry of the Republic of Belarus open up broad prospects for development and production based on these new antiseptic formulations with improved performance characteristics.

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