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Tannin Resins for Wood Preservatives: A Review

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Abstract:
Tannins and wood preservatives, in this article, are briefly introduced at beginning. The research and application progress on tannin resins for wood preservatives at home and abroad are reviewed. The significance and development prospects of research on tannins for wood preservatives are prospected.

Keywords: *Wood preservatives; Tannin resins; Research progress*

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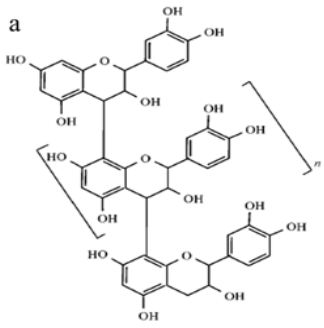
1. Introduction

Wood is one of the popular building materials at home and abroad at all times. In the era of steel and concrete, wood structure has a special charm. However, wood products are vulnerable to microbial damage during storage and use; cause a serious waste of resources, affecting their service life. It is reported that 40% of the planned wood used in the world every year is vulnerable to decay and damage by insects, with a loss of billions of US dollars. Therefore, the preservative, anti-mildew and anti-insect treatment for wood plays a key role in prolonging the service life of wood products and protecting forests.

Common wood preservatives are divided into fumigant type, tar type, oil-soluble type and water-soluble type. At present, water-soluble preservatives are one of the most widely used preservatives with various types in the world, accounting for 75% of the total amount of preservatives used. Commonly used water-soluble preservatives include chromium-copper-arsenic (CCA), ammoniacal copper quats (ACQ-B, ACQ-D), copper citrate (CC) and copper azole (CopperTriazole, RNCuAz). Although CCA preservatives have a good preservative effect, they contain heavy metals such as chromium and arsenic, which affect human health and ecological environment. It has been banned in developed countries in Europe and America. Currently, ACQ is widely used in the antiseptic industry of wood and bamboo, but the leaching resistance of ACQ is poor, and it is likely to cause certain heavy metal pollution to the environment. Moreover, the surface of wood treated with ACQ presents dark green, affecting its appearance. Therefore, it is very important to select suitable wood preservatives, which should take the damaging factors and application fields of wood into account. In this paper, the research on tannin resins, a natural and environmentally protective wood preservative, is reviewed in order to arouse the mutual encouragement of this industry and realize the development of wood preservatives towards renewable raw materials and environmental protection.

2. Tannins

Vegetable tannins, also known as a plant polyphenol, are a class of polyphenolic compounds widely existing in plants. Its yield is second only to cellulose, lignin and hemicellulose. Tannins can be divided into condensed tannins and hydrolysable tannins according to their chemical structure [1-4], as shown in Figure 1. Condensed tannins account for more than 90% of the total tannins [4,5].



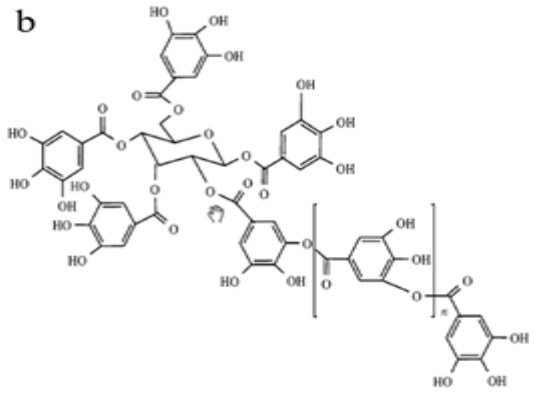


Figure 1. Molecular structure of tannins
a. condensed tannins, **b**. hydrolysable tannins

The chemical properties of condensed and hydrolysable tannins are quite different because of their completely different skeletons. The ester bonds in hydrolysable tannins are easily hydrolyzed by acids, bases or enzymes to produce polyols and phenol carboxylic acids, such as gallotannins. Condensed tannins are condensates of flavanol monomers, which are linked by C-C bonds and are difficult to decompose in aqueous solutions. The tannins contained in the bark of Larix gmelini and Acacia mearnsii are condensed tannins, which are the main raw materials for wood preservatives based on tannin resins. Although condensed tannins differ greatly from hydrolysable tannins, they also have similarities. Their two prominent common properties are complexation with proteins and metal ions and interaction with inorganic salts. The complexation characteristics of Acacia mearnsii tannins and their derivatives with metal ions (Fe^{3+}, Cu^{2+}, Zn^{2+}, Ni^{2+}) from the perspective of coordination chemistry was investigated, which provided a theoretical basis for further development and utilization of tannins [6]. In addition, tannins have certain bacteriostatic and preservative effects, and present significant inhibitory effects on many bacteria, fungi and yeasts.

3. Research review on tannin resins used for wood preservatives

3. 1 Research on antibacterial and preservative properties of tannin resins

Tannins can be directly applied for wood preservatives because of their bacteriostatic and preservative effects. Tannins belong to plant-based preservatives. Although these biological wood preservatives are green and environmentally friendly, their preservative effect is not very ideal. They need to be mixed with boron and metal salts to achieve the optimal preservative effect.

Some approaches [7-8] effectively prevented the growth of microorganisms in wood by soaking with tannin extract and treating with fixative containing c-SAA. In addition, after soaking pine wood with 4% tannin extract, 1% lead sulfate and 1% C9APE9-10, its preservative property was obviously enhanced. The antimicrobial property and its mechanism of Acacia mearnsii tannin, and concluded that Acacia mearnsii tannin had inhibitory effects on Penicillium, poplar anthracnose, canker and decay was explored. The tannins existed in alcohol-benzene extractives and had inhibitory effects on filamentous fungi was pointed out. Some specific substances (such as tannins) contained in wood itself could contribute to natural decay resistance of wood [8], but this preservative effect was weak.

Tannin resin-based wood preservatives were studied abroad in the 1970s. Hart [9] found a large number of antimicrobial components such as tannins and flavonoids in bark extracts. Subsequently, Lotz et al [10] impregnated wood with aqueous solution of vegetable tannin extract, which was treated with fixative or halogen to prevent tannin loss. When the concentration of bromine in the extract was 4-5%, it had better weather resistance, decay resistance and insect resistance [11]. Laks [12] found that condensed tannins could react directly with wood, contributing to the preservative property of wood [13]. Mitchell et al [14]. impregnated wood with 5% ethanol and tannic acid under certain conditions, and then impregnated wood with metal salt solution (40% ferric chloride) twice to resist the damage caused by fungi and termites, so as to achieve wood protection. Peter and Scalbert et al. [15-17] studied condensed tannins and found that the wood treated with additional copper, zinc, boron atoms and ammonia water had better preservative effect, which could meet the European standards for wood preservation. Moreover, Yamaguchi et al. [18,19] revealed that condensed tannin-resorcinol adducts and condensed tannin-catechol adducts could prevent decay caused by fungi. These chemically modified tannins could inhibit the growth of white-rot fungi and brown-rot fungi, and their effect was better when mixed with cuprammonium.

3.2 Research progress on tannins for fixing other preservatives

Boride has bactericidal and insecticidal properties and is harmless to human beings and animals, with good permeability and low price. Therefore, boride has long been recorded as a wood preservative. However, boride is highly water-soluble and easily lost. The research on this aspect focuses on the fixation of boride. Yu Liping [20] treated wood with the mixture of boric acid aqueous solution, gelatin and tannic acid, and found that partial boron was fixed in wood after anti-loss experiment. In addition, tannins reacted with proteins in boric acid solution to form covalent bonds under high temperature, which improved the quality of the gel and reduced the loss of boron. Patachia [21] found that metal salts (zinc, copper, aluminum, iron, etc.) also had a fixing effect on tannins.

Pizzi and Baecker [22] believed that boric acid could be used to induce the self-condensation of flavonoids and tannic acid, so that some boric acid could be stably fixed in the wood network. Thevenon et al. [23] further revealed that tannins binding to proteins could better fixe boric acid or at least significantly delay its leaching. Mazela et al. [24] found that 95% boric acid could be fixed by treating wood with protein preservatives and then tannic acid, and that wood treated with a mixture of boric acid and tannic acid could resist the attack of brown-rot fungi [25]. Tondi et al. found that tannin-hexamethylenetetramine preparation not only was a good wood preservative, but also could reduce the loss of boron. The loss of tannin-boron preparations and the preservative effect of the corresponding products were further investigated. It was found that the loss rate of boron in wood preservation based on tannins was less than 30% after a

complete leaching cycle, while the loss rate of boron preparation without tannins reached 80% [26-29]. Different tree species and tannin sources also affect the fixation of preservatives. Sen et al. [30] found that using lacquer tree tannins to treat pine wood caused a low loss rate of preservatives, and the fixation of preservatives was better after adding with 1% metal saline solution.

4. Prospects

Although plant-based preservatives are a class of green and environmentally friendly biological wood preservatives with great research value and application prospects, there are still some problems to be urgently solved, such as difficult purification, unsustainable preservative effect, high production cost, low industrial productivity and low comprehensive performance. At present, the research on wood preservatives in China still mainly focuses on the application of chemical wood preservatives, but rarely on tannin-based wood preservatives. However, with the increasing awareness of environmental protection worldwide, natural wood preservatives with non-toxicity, harmlessness, good durability, no impact on bonding properties, wide range of raw materials and low price will be paid increasing attention to, and the research on wood preservatives based on tannin resins will also become the focus of future research.

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