Review on the Discoloration Treatment Technology of Paulownia Wood

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Abstract. This paper firstly introduces different views about discoloration of paulownia wood. Secondly, it summarizes treatment methods to prevent and remove stains on surface of paulownia wood. Finally, it analyzes the trend of paulownia wood discoloration treatment technology.

1. Introduction
Paulownia is one of the important cultivation species of short-period directional industrial timber forest in China. It has a wide planting area and a large volume of timber which are widely used to produce interior decoration materials, furniture, handicrafts and other products. Every year, a large number of paulownia timber plates are exported to Japan, Korea and other countries, earning a large amount of foreign exchange for the country. Paulownia wood has many advantages, such as easy processing, elegant color, excellent dimensional stability, etc., but there is also an important defect of paulownia wood, that is, paulownia wood is easy to discolor. The discoloration of paulownia wood is the discoloration of the heartwood of mature copper-foamed standing wood and the gradual discoloration of wood during drying process after harvesting. Finally, dark brown or black brown spots appear on the surface of wood. Paulownia wood discoloration seriously affects the deep processing and utilization. In the export of foreign trade, the discoloration is forced to lower the grade and reduce the price every year, resulting in great economic losses [2]. It also has a negative impact on the production of paulownia plywood and paulownia decorative wood. The discoloration of paulownia wood is an important problem that seriously affects the processing and utilization and the healthy and sustainable development of paulownia industry in China. It has also been a scientific problem concerned by scholars at home and abroad.

The discoloration of wood has been studied in the world since 1920s and 1930s. At that time, the discoloration caused by fungi was emphasized. At the beginning of 1980s, with paulownia exported to Japan in large quantities, a great deal of economic losses caused by wood discoloration prompted wood researchers to study the mechanism for a long time and to study the application and protection methods. The long-term research of scholars in various countries has provided the discoloration mechanism and protection basis for the utilization of paulownia.

2. Discoloration mechanism of paulownia wood
There are many factors leading to wood discoloration, and the types of discoloration are complex. Generally speaking, wood discoloration can be divided into three categories: chemical discoloration, microbial discoloration and photodiscoloration. Since the early 1970s, Chinese and Japanese scholars
have made many studies on the discoloration and control of paulownia wood, and have achieved some results. Most scholars regard chemical discoloration as the discoloration type of paulownia wood, and have been trying to extract chemical discoloration substances from it. Based on these results, research on the control of discoloration has been carried out, but little progress has been made. At present, all kinds of control methods and measures adopted in production have certain effects, but it is difficult to prevent and eliminate the discoloration of paulownia wood from roots. Most scholars at home and abroad believe that the discoloration of paulownia wood is caused by the soluble extracts in the wood, but there is no final conclusion on what substances are competing for. Junqing Cheng, wood research institute of the Chinese Academy of Forestry Sciences, and others believe that the chemical discoloration of paulownia may be caused by the oxidation of polyphenols in wood by air [3]. Ping Miao's research shows that phenolic substances, iridoid glycosides and organic acids in paulownia are the internal causes of discoloration. Paulownia wood discoloration occurs when exposed to air [4]. Makino Komi of Japan and others believe that the main ingredient of reddening paulownia wood is phenolic substances dissolved in water and methanol. Japan's Dahe Yasi and others share the same with them. Ayama Akihiko believes that organic acids play a role [7]. Japan's Takamura Shinawa and Mehara Katsuo believe that the pornography of paulownia wood is similar to the photochromism of lignin model compounds [8]. Bosun Zu and others have studied the mechanism of paulownia discoloration for more than ten years, and put forward the components of inclusions which cause paulownia discoloration, and constructed the configuration reaction formula of the components. He proposed that catalpol paulownia and sesamin in wood are the main components causing paulownia discoloration, and the discoloration conditions of these components are ph, light and oxygen [9]. Tada Ruichi and others think that the discoloring components of paulownia wood are methanol and ethanol extracts, caffeic acid and sweets. Four substances were separated and their structures belong to pyranoside [10]. Delong Chang of the Paulownia Research and Development Center of the State Forestry Administration mainly studied the discoloration of paulownia wood from the point of view of microorganism. It was considered that the discoloration of paulownia wood was microbial discoloration, and the two kinds of discoloration fungi of paulownia wood were streptomyces and a rhizopus [11].

3. Treatment of paulownia wood discoloration

At present, the prevention and control methods used in production and studied in laboratory can be divided into two categories according to the purpose: one is color change prevention, the other is decolorization treatment.

3.1. Prevention of paulownia wood discoloration

Anti-discoloration treatment of paulownia refers to the treatment of wood without discoloration until the color changes after sawing. At present, there are many studies on the prevention of paulownia wood discoloration. There are three main methods: one is to dissolve discoloration components in wood by soaking in solvent, i.e. using water as solvent. Secondly, wood is treated by chemical method, that is, oxidant or reductant, which can decompose the discolored components or change the structure of the chromogenic groups of the discolored components, and acid or alkaline chemicals can be used to treat the wood to change its structure so as to achieve the purpose of anti-discoloration [12]. Another method is the combination of physical and chemical methods, i.e. water solution combined with chemical reagents to treat paulownia wood[11].

3.1.1. Solvent immersion method. Solvent immersion method can be divided into normal temperature, variable temperature, atmospheric pressure, pressure decompression, hydrostatic and flowing water immersion methods according to the change of temperature and pressure and whether the solvent flows or not.

- Natural dissolution method. This method has a long history and is a traditional method before industrialized treatment of paulownia wood, i.e. to stack logs or boards in the open air and let the wind
and rain drip, so that sap in the wood moves to the surface with water. It usually takes 6-12 months or more to reuse the stains on the surface of the wood. The method is simple and can not only stabilize wood properties, but also be advisable from the point of view of preventing discoloration after processing. But the turnaround period is too long, and because the stain penetrates into the wood, the energy consumption is more when shaving, which can not meet the needs of large-scale industrial production.

- Normal temperature and pressure immersion method. This method is currently used in domestic paulownia plate processing plants. The general practice is to saw raw wood or logs dried for a period of time into boards with thickness of 20-25 mm and unlimited length and width, stack them closely in a cement pond, press heavy objects, then submerge them by irrigation, soak them at room temperature for 10-15 days, and change water 2-3 times in the middle. Because the water temperature depends on the temperature of the climate, the soaking period and the soaking effect change greatly. In summer, the soaking period can be shortened appropriately and the effect is better; in winter, the water temperature is low, even if the soaking time is prolonged, the effect is not ideal. The advantages of this method are simple, energy-saving and no heating equipment. The disadvantage is limited by the climate, no man-made changes in the soaking conditions, relying on experience to determine the soaking time, can not be quantitative control of the effect of soaking and the quality change is large.

- Atmospheric pressure variable temperature method. The wood utilization group of the department of landscape architecture of Henan Agricultural College has carried out the experiment of soaking different kinds of paulownia wood under atmospheric pressure and variable temperature, that is, soaking different kinds of paulownia wood with water of different temperatures, such as paulownia lankao, for about 5 days, then soaking with hot water of 900 degrees for 24 hours, while paulownia tomentosa is soaked in hot water below 700 degrees, while paulownia alba is soaked in water above 800 degrees, with better results. From the experimental results, the effect of variable temperature soaking is better than that of normal temperature soaking. The problem is that this method must increase heating and insulation facilities, consume a lot of heat energy, and the cost of production will inevitably increase [11].

- Decompression method. That is to say, in a sealed container, paulownia wood is first sprayed with water to make it wet, then vacuum is pumped, and the water in the wood and the discolored components dissolved in the water are extracted by negative pressure. So many repetitions, so as to achieve the purpose of preventing paulownia wood discoloration. This method was first applied to paulownia wood in 1980 by Makino Komi, and a set of special equipment was designed. It is reported that good treatment effect has been achieved. In addition, some people in China are also engaged in this aspect of research work. The advantage of this method is that it has short processing period, good effect, can be controlled artificially, and is not limited by climatic conditions. The disadvantage is that the equipment has a higher requirement, and it needs to consume a certain amount of electric energy in the process of operation. It is also difficult to use it on a large scale in production.

- Immersion extrusion. This is the method invented by Aoshan Qingyan. First, paulownia sheets pass through the suction pool, suck up enough water or treatment liquid, and then squeeze out the sucked liquid through a number of pairs of extrusion rolls, pressurizing on both sides. This is repeated until most of the discoloration is removed. The advantages and disadvantages of this method are similar to those of the decompression method. Because of the higher equipment requirements, the equipment investment is larger.

- Running water immersion method. Paulownia plate is immersed in flowing water, essentially the same as the static immersion method in the pool, but because of the continuous dilution of flowing water, the discolored ingredients are taken away by the water as soon as they dissolve, unlike the latter, when the concentration of discolored ingredients in the pool reaches a certain value, the immersion effect is better than the latter. This method uses a large amount of water, only in mountain streams with sufficient water, and is limited to soaking a small amount of wood. If soaked in large quantities, the concentration of the extract in water will probably be too high, causing pollution and other problems.
The above methods are all trying to dissolve the discolored substances in paulownia wood by soaking in order to prevent the discoloration of wood. These methods have a certain effect on preventing the discoloration of paulownia wood surface, but have little effect on deep wood. The reason is that there are many discoloration components in the wood, and it is impossible to dissolve all discoloration materials. Therefore, the above methods can not change the development of the discoloration process of paulownia wood.

3.1.2. Chemical treatment method. Research on chemical methods to prevent paulownia wood discoloration is being explored at home and abroad. There are mainly the following methods:

- Oxidation process. Paulownia wood was treated with 10% hydrogen peroxide and 0.1 N sodium hypochlorite [13] to decompose the discolored components, which had a good effect on preventing the discoloration of paulownia wood. But these strong oxidants oxidize the main structural components of wood, especially lignin, which destroys the integrity of wood to a certain extent and reduces its strength greatly. At the same time, they also oxidize and decompose the pigments other than the discolored components, making the treated wood very white and the original texture level disappear. It lacks the unique color of natural wood. Therefore, it is generally not advisable to use strong oxidant treatment to prevent discoloration. It is only suitable for bleaching on a very shallow surface, i.e. to change the uneven color of wood before painting.

- Reduction method. Paulownia wood was immersed in 1.5% oxalic acid and 1.1N sodium thiosulfate solution. These reductants have some effect on eliminating the stain on discolored wood, but they can not prevent the discolored wood from discolored, because the role of reductants is to reduce the colored chromogenic groups (oxidized products) to colorless groups. It is obviously inappropriate to add reductants before the formation of chromogenic groups. Moreover, when discoloration occurs, whether the reduction ability of these reductants can reduce the discolored substances to colorless components remains a question. Even if the reducibility of the reagent is strong enough, the discolored substances can be reduced to colorless ingredients, which will be oxidized again in the future under the action of air, resulting in the so-called "discoloration" of wood. In this sense, whether it is appropriate to treat discolored paulownia wood with reductant remains to be studied.

- Other modifiers acting on discolored components. Paulownia sheets were coated or immersed in 5% amino pulse, 10-30% urea, 2% borax and 2% boric acid solution, which had different effects on preventing red discoloration. Makino, etc. considered that immersing in 10% urea water solution for 48 hours could effectively prevent discoloration, and treating with 5% semicarbazide was effective, but the treated wood would turn yellow in the process of placing. The treatment with 2% borax and boric acid is not as effective as the first two agents. The semicarbazide can inhibit the discoloration caused by thermal action to some extent[15]. Urea inhibits enzymes involved in discoloration [3]. Boron compounds can form complexes with some polyphenols and change their properties. Misaki Sato and others also treated with formaldehyde aqueous solution, the effect is not obvious [16]. Bosun Zu immersed the samples in polyethylene glycol aqueous solution. It was found that after 2-3 months of treatment, the wood had light color and good gloss, but after 3 months, the surface of the plate began to yellowing, which had some similarities with that treated with semicarbazide [15].

- Soak in acid, alkali, etc. Wood utilization group of the department of landscape architecture of Henan Agricultural University and Sato Teng-ku have all done soaking experiments with sodium hydroxide solution. The latter also used 0.1N hydrochloric acid and 1N acetic acid to carry out experiments. They all think that alkali treatment has certain effect. So far, various attempts have been made to prevent the discoloration of paulownia wood by chemical treatment.

3.1.3. Physicochemical combination Method. The physicochemical method is to treat paulownia wood with water solution (physical method) and chemical reagent. The chemicals used are all mild chemicals, which will not cause damage to wood, safety to human, livestock and environment, and will not cause environmental pollution. Sodium bisulfite was used to inhibit the activity of enzymes
and reduce the degradation of wood. Sodium carbonate was used to change the PH value of wood, inhibit fungi and depolymerization enzymes. Borax was used to sterilize and inhibit bacteria. The formulation of these three reagents had a good effect on preventing wood discoloration [11].

3.2. Decolorization of paulownia Wood
Decolorization of paulownia wood refers to the removal of color spots on the surface of paulownia wood. There are many decolorization methods, which can be summarized as follows [12]:

3.2.1. Cold water immersion method. The paulownia timber soaked in this method has a long time, and the decolorization effect is not good because of the low temperature.

3.2.2. Warm water immersion method. This method is conducive to the dissolution of the inclusions, and the soaking time of tung wood is short. In order to improve the decolorization effect, it is necessary to replace 2-3 times of water in the middle.

3.2.3. Solvent immersion method.
- Oxidation process. Paulownia wood is immersed in a certain proportion with petroleum ether and ethanol (1:1). Although this method has certain effect, the organic agent is volatile and flammable, which causes great pollution to the environment and is unsafe.
- Reduction method. Dilute hydrochloric acid (0. lmol / L), dilute sodium hydroxide (0. lmol / L), dilute oxalic acid, dilute ammonia water and other solutions were soaked or brushed with hydrogen peroxide. Although some of the spots can be eliminated by the above methods, they will reappear soon.
- Other modifiers acting on discolored components. The discolored material was treated with a comprehensive formula including decolorizer, penetrant, anti-discolorer and inhibitor. This method is used to treat the test material and determine the color of the treated material for one year. After treatment, the color of the treated plate is natural, bright and has a certain depth of treatment, which can make the grade-II material jump to the grade-II material and reduce the number of grade-III material.
- Soak in acid, alkali, etc. At present, the most effective method is to decolorize the discolored paulownia after permeability improvement by using a combination of chemical reagents. Firstly, through the comprehensive analysis of the brightness, redness, edge scarcity, total color difference and whiteness of the samples before and after one year, the optimum decolorization treatment formula is 1%H2O2, 0.05%NaHCO3, 0.1%NaHSO3 and 0.05%C18H29NaO3S. The test results showed that the color value of discolored hybrid paulownia after decolorization, except redness, and yellowing degree, had no significant difference with the redness of grade A board exported from foreign trade (except that it could meet the standard of grade A board). The other color values were better than grade A board exported from foreign trade, with a significant difference of 99%. By using the optimum decolorization formula to treat 2.1 m³ hairy-edged discolored hybrid paulownia board and process it into finished products, the test results show that it can bring new economic benefits of 2014.58 RMB/m³. In addition to better economic benefits, it can also expand the industrial use of hybrid paulownia, change people's ideas about the difficulty of decolorization and poor grade of hybrid paulownia splints, and promote the cultivation and planting of fast-growing and high-yielding hybrid paulownia, which has good social benefits [11].

4. Conclusions
Paulownia is the main fast-growing artificial timber forest species in China. It is widely planted, accumulated and used in furniture and building materials. Its discoloration control is an urgent technical problem to be solved by production and scientific research departments. From the physical structure and chemical composition of paulownia wood to study the influence of anatomical characteristics and chemical characteristics of its inclusions on discoloration, to the evolution of microbial discoloration, it reflects the rich achievements of researchers at home and abroad at different
stages. With the mature application of UV inkjet technology in different interface materials, spraying paulownia normal texture pattern on paulownia discolored surface is also the direction of attempt, but this technology is more suitable for the treatment of final surface effect of paulownia products rather than substrate surface. At the same time, texture ratio effect, technical operation difficulty and implementation cost are all worthwhile consideration of important factors. There are differences in discoloration mechanism and treatment methods among different regions and tree species of paulownia. From treatment technology to prevention, the methods of discoloration of paulownia have been constantly improved. It is necessary to conduct systematic and in-depth re-study on how to combine new technologies with interdisciplinary platforms, and select appropriate methods to reduce and reduce discoloration of paulownia wood in order to improve economic benefits.

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