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NEW MATERIALS TO SUPPORT THE PRESERVATION OF OLD WOOD USED FOR ART OBJECTS

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ABSTRACT

This paper presents new materials that replaced the main list of substances with a high toxicity level (banned in the European Community), and the interventions in the preservation of old wood used for art objects. Although in the process of stopping the four evolutionary effects of deterioration and degradation of the wood, highly effective methods of preservation were developed, it was found that the toxic atmosphere maintains a high risk for curators. These methods involved the use of derivatives of naphthalene and polymers containing chlorine, bromine-based derivatives, namely a series of highly dangerous pesticides. In this context, most research centers in wood preservation have studied new systems supposing minimal toxicity, compatible with different types of timber, in a series of natural or synthetic substances, such as: Pyrethroids, boron compounds, tannins, woodsulfonates, silicates and phosphates.

KEYWORD: wood, preservation, restoration, toxicity, pesticides, environmental pollution

1. Introduction

The wood, as a structural or ornamental element from within the composition of cultural treasures, is an organic material with low resistance over time. It is known that the environmental and climatic factors, such as heat and fuel sources, microorganisms, acid rain and not lastly the man, lead to a series of micro and macro structural destructions and evolutionary alteration, translated by two effects: deterioration of structural-functional elements and degradation of the basic constituents, lignin and cellulose. To that effect, in order of their frequency and aggressiveness, we mention: putrefaction, carbonization, career, embrittlement, discoloration, waiving, cracking/fracture etc.

Treatments to preserve old or new such wood, most of the times, stop synergistically most of the above processes, using a number of substances as such or as organic dispersions (solutions, emulsions, gels soils etc.) which are toxic or produce unwanted effects on the environment and the operators. Because of that, at present, the subject of active products and solvents involved in these treatments and having a minimal impact on the environment is of great interest for many research institutions. Surface water and groundwater with soils in the immediate vicinity of the areas or treatment facilities are mostly affected by these treatments.

Consequently, we face, on the one hand, the problem of soil and air remediation, wastewater treatment, surface water and groundwater treatment to meet drinking water quality criteria, and, on the other, the selection of most environmentally friendly treatment solutions, involving the cheapest processes and technologies [3-6].

Therefore, the research of new treatment systems of highly toxic substances (polymers and naphthalene derivatives containing chlorine, bromine derivatives, and a series of pesticides) banned by the regulations of the European Agency for Registration, Evaluation and Authorization of Chemicals (REACH) will be taken into account [7].

2. Evolution of degradation and deterioration effects on wood

The experts identified four major types of degradation and deterioration effects on wood: physical (cracking, fracturing, waiving, bending, displacement, swelling, shrinkage), physichochemical (change of color and organoleptic characteristics because of enzyme attack, radiation or heat exposure, desorption, chemical composition changes as a result of microbiological activity, change of normal range of variation of the hydrous equilibrium under the influence of climatic factors), biological (annual rings contraction, cracking, embrittlement, rotting), functional (reduced or loss of functional and artistic role of the artwork, transformation into a source of pollution for the environment) [1].

Table 1 presents in detail the degradation and deterioration effects, with the associated processes.

Tabel 1. *Most important processes responsible for deterioration and degradation effects of old wood used for art objects* [8]

Deterioration and degradation effects	**Process**
Putrefaction	Biochemical (enzyme or not)
Carbonization	Thermal combustion (burning)
Radiation degradation	Radiolysis and photolysis
Career	Wood decay attack (bio deterioration and biodegradation)
Molding	Fungal attack (bio degradation)
Embrittlement by β-glycosidic hydrolyse or solubilization of the fragments of cellulose and lignin	Fungal attack + biochemical attack + chemical attack (acidic, alkaline or saline and oxidant)
Color change	Fungal attack, chemical or photochemical
Swelling/shrinkage/waiving/twisting	Mechanical
Cracking/fracturing/splinting	Mechanical + chemical + bio chemical
Fossilization/mineralization	Chemical + biochemical + geochemical

To replace old wood treatment recipes containing highly toxic substances, research centers offer insectofungic systems, fireproof systems, hygrophobic systems, stabilized dimensional systems, based on pyrethroids, boron compounds, tannins, lignosulphonated, silicates and phosphates and synergistic systems with multiple effects.

3. Insectofungic systems

Insectofungic systems have the role to protect or to stop, minimize and remove the effects of microbiological attacks by xylophagous insects, molds, fungi, mushrooms, and others. The most used and most freqeuntly mentioned in literature are the insectofungic compounds containing boron [9, 10]. They are considered multipurpose pesticides (insecticides, fungicides, herbicides etc) and provide nearly 100% protection for heritage objects [11]. Among the boron compounds, mention must be made of synthetic boric acid mixed with glycerin, borax, sodium metaborate, which is the most widely used. A selection of synthetic pyrethroids for insectofungic wood treatment should include: permethrin, deltamethrin, bioresmethrin, cypermetrin. The following organophosphorus insecticides may be used: chlorpyrifos, fenthion, dichlorvos, fenitrothion, malathion, diazinon, triclorfon.

One of the insectofungic procedures in treating wood is to obtain a pesticide emulsion or other formula dispersible in water, with an average particle size of 200 nm. The treatment is particularly effective in protecting wood and timber against common insects (Anobium punctatum, Xestobium rufovillorum), Longhorn pets (Hylotrupes bajulus), dry rot (Serpula / Merulius lacrimans) and wet rot (Coniophora puteena) [12].

Another wood treatment material was used with a synergistic insecticidal action that includes compounds of boron and synthetic pyrethroids. This combination has proved to be particularly effective in conferring resistance to insect attack, with the most cost-effective report in terms of Formosan termites [11].

Another type of insecticide has the form of a dissolved pyrethroide up to saturation into a fluid such as carbon dioxide. The composition may include a co-solvent such as methanol. The treatment method consists in impregnating the wood with this composition and reducing the temperature and pressure under the critical level of the insecticide timber precipitation [13].

Among synthetic pyrethroids, in mixtures with boron derivatives, the following are also used:

- permethrin, an environmentally friendly product, with effective action to halt microbial attack, but also dimensional stability and does not affect or polychrome layer preparation;
- deltamethrin, with median lethal toxicity (LD50 = 135-5000 mg/kg live weight);
- bioresmethrin, decomposes under the action of UV radiation, rapidly hydrolysed in basic medium, median lethal dose (LD50 = 707-800 mg/kg live weight);

- cypermethrin, a non-systemic insecticide with contact and ingestion action (product toxicity - LD50 = 250-4150 mg/kg live weight).

Among organophosphorus insecticides in mixtures with synthetic pyrethroids and/or boron derivatives we would like to mention:

- chlorpyrifos, with a moderate toxicity to vertebrates (LD50 = 135 mg/kg live weight); it is a non-systemic insecticide with contact and ingestion action, that can also act as vapors;
- fenthion, contact and ingestion insecticide with big shock action and good persistence; it is an effective larvicide, with a medium toxicity to mammals (LD50 = 215-316 mg/kg live weight);
- dichlorvos, an insecticide with contact and ingestion action, has an action of shock; its remanence is reduced owing to the great volatility; recommended for Disinfection DDVP indoors. It is a powerful inhibitor of cholinesterase and has a high toxicity to mammals (median lethal dose LD50 = 62 mg/kg live weight);
- fenitrothion, stable to hydrolysis in acidic medium, neutral and basic;
- malathion, an insecticide contact and ingestion, breathing with low action. It has a broad spectrum of activity and a low toxicity to mammals (LD50 = 1300-2800 mg/kg live weight);
- diazinon, an insecticide good contact, ingestion and respiration, has a large share of shock, is also a good acaricide. It has a relatively high toxicity to mammals (LD50 = 108 mg/kg live weight).

4. Fireproof systems

Fireproof systems strengthen the wood fibers to withstand the larger and more frequent variations in temperature than the normal range. The recipes we used are based on inorganic compounds, metal oxides or insoluble salts (fine powders of ZnO, CaO, TiO_2, Sb_2O_3 [14, 15, 16], talcum or micronized asbestos, thermal ash, chalk powder, plaster, colloidal barite, silicon dioxide, zeolite or colloidal volcanic tuffs [17], dry metal sludge, etc.), in mixtures or dispersions that can be diluted with water, usable only inside buildings, as water paints, not to protect exterior surfaces exposed to weather factors.

For fireproof wood protection we also use water soluble products based on boron, ammonium, sulfate, phosphate, silicate etc. salts, and products that form films or coatings on the surface (thermofoaming paints and other products generating inert gas or inert steam or hot melt products, making the fireproof process) [18-20].

Thus, the most widely used system for protecting wood and wood construction materials is the aqueous dispersion based on ammonium phosphate and ammonium sulfate or boric acid and sodium fluoride. These products have a good fireproof action but a small antiseptic action, while having a pronounced corrosive action on metals, causing degradation of joint elements and of metallic reinforcement after application.

Protection products soluble in water and based on soluble salts of copper, chromium, fluoride, boron, arsenic, ammonium, phosphate, silicate etc. have the disadvantage that they produce the rewetting of elements.

5. Hygrophobic and dimensional stability systems

Hygrophobic systems ensure a significant reduction of the hydrophobic character of the wood, so typical of this material. The coated systems the wood fiber retains a constant size in the presence of water.

This feature is very important to achieve the other effects of preservation, because any wood treatment system is based on a liquid.

A very important treatment for the elements located in humid climates or for those exposed to the weather, includes higher hydrocarbons (paraffin), waxes, natural and synthetic resins [21].

Wood treatment with calcium silicate significantly increases its resistance to humidity, deformation, and ensures environmental protection, having a very low cost of implementation [22].

To treat wood with a very low degree of permeability to a preservation agent, we mention the injection method under pressure (from 0.08 mA to 1.2 mA) of an aqueous solution of an antibacterial agent containing quaternary ammonium salt and polyalkyleneglycol, with 8 as pH minimum value [23].

6. Materials and methods of preservation with multiple action

A number of processes and technologies for wood treatment are known to use for insectofungic and fireproof action different tar and petroleum products as such, or as macerated containing extracts from various plants such as oak tannin, chestnut glucosides, conifer terpenes etc. [13, 24, 25].

Old traditional technologies based on oil, mainly used to treat wood for construction, furniture, carpentry, floors, paneling etc., are intensely discussed today although they gave good results. Their weaknesses are due to the staining of wood and to creating artificial skates to polychromy.

Red oil has some great features, such as very low density and viscosity, flammability and high evaporation rate, a very small concentration in solid paraffin (colorless or white), an enough high concentration of aromatics and other products, and a good ability to extract active ingredients from plants or other natural products by maceration at room temperature.

Of all organic systems containing red oil in various active ingredients the following are very effective in treating wood: pentachlorophenol, sodium pentaclorfenolat (PCP-Na), copper pentaclorfenolat (PCF-Cu), silver pentaclorfenolat (PCF-Ag), lindane.

Propolis is presented as a heterogeneous mass of resin with a solid consistency, sometimes compact and waxy due to malleable and adhering particles, sometimes granular or friable, taking the appearance of powdery debris. This composition, which shows some strength at ambient temperature, becomes friable at low temperatures, below 15°C, even for waxy ways. It is insoluble in water and soluble in alcohol, acetone, ether, chloroform, propylene, benzene, dimethylsulfoxide, ethylenediamine. Depending on the temperature, the dissolution rate varies and so does the passing or not in solution of some fractions to, for example, wax that dissolves in hot alcohol, but is hardly soluble in cold alcohol.

Mainly resins, waxes, volatile oils, pollen, carbohydrates, amino acids, vitamins, enzymes, mineral salts and impurities have been reported in the chemical composition of raw propolis.

Tannins are polyphenols substances (derivatives of 3-hydroxy-flavan or polyesters of gallic acid) soluble in water, gusto astringent, which are reactions characteristic of phenols and alkaloids and precipitated with protein, forming waterproof and rot-proof combinations. As types of relationship between polyphenols and phenolic acids we can consider: hydrolyzable tannins and condensed tannins or unhydrolyzed.

Among synergistic systems with insecticide and firepoof action, impregnations with protective agents are widely used. In the past, copper arsenite water based and pentachlorophenol and creoset oil based were used with protection effect against biological deterioration. As inflamed agents were used phosphates, ammonium salts, bromides, ammonium oxide were used as inflammable agents. Colloidal aqueous solutions with silicon dioxide were used against pest appearance and development [26].

A method of treating wood with multiple protection action against aging, mildew and degradation by ultraviolet light contains zinc oxide in combination with salt dimetilalchilamină monocarboxylic acid [27].

A treatment with fireproof and antiseptic role contains a fireproof substance based on an aqueous solution of diammonium phosphate, ammonium sulphate and a humidifier, and an insecticide in the form of an aqueous solution of poly-hexamethyleneguanidinephosphate chloride [28].

The wood treatment laboratories can also provoke soil pollution by products of Cu, As, Cr; soil electrodialysis in distilled water or in an aqueous solution of HNO_3 effects pollutant cleaning simultaneously [6].

Another method for wood residue preservation uses polycyclic aromatic hydrocarbons (PAHs) and As, high molecular weight products; its extraction from soil by aerobic biodegradation was carried out [6] and its concentration is evaluated with sequential extraction. Under the action of a nonionic surfactant, the degradation of PAHs with both low and high molecular weight was obtained. The negative effect of this method is its increased toxicity as a result of microbial activity. For the near future, the use of standardized tests using the bacterium Vibrio eco Fischer (Microtox ®) is anticipated.

Conclusions

There is a constant concern for finding more multiple action treatments able to ensure the conservation of wood. Synergistic wood treatment should be less polluting for the environment and for the human factor working to turn the wood used for art objects more resistent to degradation as a complex of environmental factors.

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