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Elaboration of a composition based on spent engine oil and wood flour for birch wood impregnation and railway sleepers production

L I Belchinskaya, K V Zhuzhukin, A I Dmitrenkov, L A Novikova and N A Khodosova

Federal State Budget Educational Institution of Higher Education "Voronezh State University of Forestry and Technologies named after G.F. Morozov", 8 Timiryazeva str., 394087, Voronezh, Russian Federation

E-mail: chem@vgltu.ru

Abstract. The "hot-cold baths" impregnation of birch wood samples by a number of oils (original engine oil, waste motor, spent transmission, spent corn and sunflower oils) were studied in order to choose a base for impregnating composition. Specimens of wood flour from coniferous and hardwood species, oak, birch and pine bark were used as fillers of impregnating compositions. Physical-chemical characteristics (absorbed amount of impregnated compound, water absorption, swelling in tangential and radial directions, wetting angle) of wood samples treated with impregnation compositions were determined and compared to the most common oil antiseptic ZHTK-2. A strong decrease of water absorption and swelling of wood samples was observed for birch wood samples impregnated composition on the base of spent engine oil. Use of softwood flour as a filler of impregnating composition caused stronger enhancing of wood hydrophobicity, mainly, due to abietic acid dissolution in spent engine oil. 1 w.% of softwood filler of the impregnating composition was found the optimum providing the wood shape and water stability. The developed composition is recommended for impregnation of birch wood to be used in railway sleepers production.

1. Introduction

Wooden sleepers [1] are mainly used for railway and tram tracks [2], subways, access roads to production facilities, logging tracks. Nevertheless, there is a tendency to replace wood sleepers with reinforced concrete ones, since they have a longer service life and are mechanically stronger [3]. However, the need for wood sleepers is still high, as reinforced concrete sleepers have several disadvantages that do not allow their use in a certain area and for a particular climate [4,5]. These include a large mass, fragility, rigidity, limited corrosion resistance, electrical conductivity, high cost, and the possibility of fatigue failure of concrete [6]. Therefore, the use of wooden sleepers in some cases remains relevant [7]. Wooden sleepers are mainly made of commercial pine wood, the reserves of which have been significantly reduced, both in Russia and all over the word. In this regard, it is advisable to use wooden sleepers made of hardwood, including birch. Birch wood has low cost and is the most common tree species in the European part of Russia and Siberia. The area of birch forests in Russia is about 80 million hectares with a total stock of industrial wood of about 6 billion m^3. Birch is diffuse-porouscoreless species with a homogeneous wood and high physical and mechanical properties, i.e. high strength (especially under shock loads), hardness, wear resistance. Due to the features of the structure, birch belongs to well-impregnating species. Birch density is 650 kg/m^3, increasing at a moisture content of 12% up to 670 kg/m^3), whereas that of widespread in Russia pine is 520 kg/m^3. Birch wood is characterized by a low resistance to decay, which develops due to the presence of *Nyctomyces suaveolens* fungus [8].

To increase the service life of softwood sleepers, as a rule, they are subjected to impregnation [9]. In particular, oil formulations are used for protecting of wood from decay [10].

Traditionally, wood sleepers are impregnated with coal oil [11, 12]. However, this impregnating oil is highly dangerous (second hazard class), has a relatively low pour point (from -2 to -5 °C) and a tendency to form precipitation. Therefore, a more environmentally friendly impregnating composition of ZHTK type [13] of lower low-hazard (fourth hazard class) was developed. However, this antiseptic is rather expensive. Firstly, one of the fractions of the composition is used to produce diesel fuels. Secondly, this composition must be filtered, removing mechanical impurities, which complicates the process.

Spent engine oils (SEO) are foreseen to have large potential opportunities in wood impregnation applications, since they possess antiseptic properties, less dangerous (fourth hazard class) [14] and cheap. According to AUTOSTAT data, the consumption of motor oils by passenger cars in Russia reached 232 million liters per year in 2018 and will reach 245.8 million liters per year till 2023. Despite significant and increasing amount of SEOs, their utilization does not currently have an industrial scale. The problem of SEO utilization in the state can be solved by the use of SEO in impregnation compositions of wooden of railway sleepers, which is of high scientific interest and promising practical area.

The purpose of this work was to develop an impregnating composition of birch wood samples providing enhanced water resistance and shape stability of wood for its further application in railway sleepers production.

2. Methods and materials

In order to develop an impregnating composition for wood, first, a selection of an oil base was carried out. For this, a number of oils were tested, including original engine oil (EO) from “LLK-International” Ltd, Russia; spent engine based on distillate oil (SEO), spent transmission oil (STO) Lukoil 80W90 TM-4 (“LLK-International” Ltd, Russia), spent sunflower oil (SSO) “Semilukskaya trapeza” from “Semilukskii pische kombinat” Ltd, Russia, spent corn oil (SCO) “Altero Beauty” (OJSC “EFKO”) and a conservation liquid ZHTK-2 (Ltd “Oktan”, Russia).

As a filler of impregnation composition wood flour of coniferous (WFC) and hardwood (WFH) species, flour of oak bark (FOB), birch (FBB) or pine (FPB) supplied by OJSC “Radovitskii wood working plant”, Moscow, was introduced. The ratio of SEO and wood flour (or flour of wood bark) was 99.5-98.0 w.% and 0.5-2.0 w.% correspondingly. The size fraction of the filler varied from 10 to 30 μm.

For the selection criteria of a base for impregnation composition were chosen the following ones: low cost, availability, environmental friendliness and high antiseptic characteristics. The impregnating compositions were evaluated according to the following physical parameters of wood samples: amount of impregnating composition 9impregnant) absorbed by wood [15], water absorption for 30 days in distilled water [16], swelling in the tangential and radial directions [17].

2.1. Wood samples impregnation

For impregnation, birch wood (BW) specimens (20×20 mm size in radial and tangential directions, 10 mm along the fibers)cut out from the 12-year-old birch tree of experimental forestry of Voronezh State University of Forestry and Engineering, Voronezh, Russia were prepared. Samples were cut from the middle part of the trunk at a height of 1.3 m, at a distance of 0.1 m from the center of the trunk.

The impregnation was carried out by the method of "hotter-cold baths". The impregnating composition was heated to a temperature of 120 °C, into which the samples were placed and kept for 20 minutes, then transferred to an impregnating composition having an ambient temperature for the next 20 minutes. For each group of experiments, at least 10 samples were used.

As a result of heating of the oil (SEO) to a temperature of 120 °C and immersion of wood specimens into this solution, oxygen molecules present in wood structure oxidize oil hydrocarbons [18]. A small number of water molecules form an emulsion solution, released some free space in wood structure for the impregnating composition, which penetrates into the volume of wood specimen as a result of diffusion and capillary processes.

The replacement of hot oil with cold one causes a drop in pressure in the cell cavities due to compression of the air contained in them and vapor condensation. The pressure of a cold liquid is equal to atmospheric and it turns out to be higher than the vapor pressure in cavities of wood cells. As a result of the pressure drop, wood is impregnated. It is obvious that the speed of molecules movement of cold oil hydrocarbons is much lower.This makes a condition for the pressure drop and, thus, for intensification of the impregnation process. In addition, molecules of cold oil act as a barrier and impede the release of hot oil molecules from wood.

2.2. Water absorption by wood measurement

To determine water absorption, wood specimens were dried at 105 °C in weighing glasses untilconstant weight, placed in a desiccator under the porcelain grate and coveredwith distilled water. After 1, 10, and 30 days specimens were weighed.

The amount of absorbed moisture was calculated by the formula 1:

$$W = \frac{m_n - m_1}{m_1 - m} \cdot 100,[\%] \tag{1}$$

where m_n - mass of weighing glass with specimen, g;

m_1 - mass of weighing glass with specimenin absolutely dry state, g;

m - mass of weighing glass, g.

2.3. Swelling of wood determination

Wood swelling was assessed via measurementof their sizes in the tangential and radial directions using calipers with an accuracy of 0.01 mm. Samples used to determine water absorption for 1, 10 and 30 days were removed from the desiccant with distilled water and tested for size change.

The values of wood swelling in tangential and radial directions were calculatedapplying expressions (2) and (3).

$$a_t = \frac{L_{t\max} - L_{t\min}}{L_{t\min}} \cdot 100, [\%] \tag{2}$$

$$a_R = \frac{L_{R\max} - L_{R\min}}{L_{R\min}} \cdot 100, [\%] \tag{3}$$

where $L_{t\max}$, $L_{R\max}$ - size (mm) of samples after water absorption for 1, 10, 30 days in tangential ($L_{t\max}$) and radial ($L_{R\min}$) directions, respectively;

$L_{t\min}$, $L_{R\min}$ - size (mm) of samples in absolutely dry state in tangential and radial directions, respectively.

2.4. Wetting angle determination

Good wetting of wood samples is required for efficient wood impregnation. The rate of wetting of birch wood with mineral engine oil was determined by the magnitude of wetting angle.

To measure the wetting angle of wood specimens, a liquid drop method was used. It is based on measuring the contact angle of a liquid drop on the surface of a solid body. A drop of motor oil was pipetted onto a smooth surface of the birch wood samples, kept for some time until the droplet spreads (at a temperature of 20 °C) over a hard surface and the equilibrium is established.Then, the samples with a drop was placed in a slide projector [19] between the lens and the light source. The contour of the drop was projected onto a screen, providing 15 times magnified image of the drop of the test liquid on wood surface. To the contour drawn on a sheet of paper

A tangent is madeat the contact point of three phasesin the direction of liquid phase to the contour of the drop drawn on the paper. The wetting angle between the tangent and the solid surface is determined by the protractor or, more precisely, wetting angle (tgθ) is calculated using the formula:

$$\mathrm{tg}\theta = \frac{2\mathrm{hr}}{\mathrm{r}^2 - h^2}, \tag{4}$$

where h - height of drop in the contour, mm, r - radius of drop sphere, mm. The value of θ were taken from three parallel measurements.

2.5. Assessment of molecules size of spent motor oil

To determine the possibility of diffusion of the SEO molecules into wood, it is necessary to know the sizes of its structural components and the size of oil molecules. Different arrangement of structural elements of wood creates a layered structure of the cell wall, i.e. microfibrils. These tape-like formations have a thickness of 5-10 µm, a width of 10-30 µm, a length of several micrometers and include elementary fibrils. Sometimes larger structural formations are seen that are visible in a conventional light microscope. These are so-called macrofibrils, or simply fibrils, having transverse dimensions of about 400 µm or more.

According to [20,21], the diameter of large vessels varies from 0.2 to 0.4 mm, small ones - from 0.016 to 0.1 mm, along which there are numerous pores. Libriform fibers have a diameter of 0.02-0.05 mm with small pores on the walls. The size of parenchymal cells ranges from 0.01 to 0.1 mm. The diameter of the prosenchymal cells is in the range of 0.01-0.05 mm; their length is 0.5-3 mm. The value of birch wood porosity ranges from 40-70%. It depends on many parameters.

The size of the motor oil molecules was determined by the known method [22]. A drop of used engine oil was applied to the distilled water in a 1.0×1.0 m vessel. The oil spread over the surface of the water and a round spot was formed. After the drop stopped spreading, the diameter of it in two mutually perpendicular directions was taken and the average value of oil spot diameter was determined. Then the spot area was calculated by the expression (5)

$$S_{\mathrm{spot}} = \frac{\pi \cdot D^2{}_{\mathrm{drop}}}{4} \ [\mathrm{m}^2], \tag{5}$$

where D_{drop}– diameter of spread oil spot.

The diameter of the motor oil molecule was determined by the formula (6)

$$d = \frac{V_{\mathrm{drop}}}{S_{spot}} \ [\mathrm{m}], \tag{6}$$

where V_{drop}– is the volume of a drop of engine oil, m^3; S_{spot}– area of oil stains, m^2.

3. Results and discussion

Table 1 summarizes characteristics of birch wood samples treated by a number of spent oils in order to select an oil base for the development of an impregnating composition. The effectivity of impregnation was taken as a criterion for the selection of oil as a base against the following indicators: amount of impregnating composition absorbed, water absorption by wood and wood swelling in tangential and radial directions.The obtained data were compared with ZHTK-2, the most common oil antiseptic for impregnating railroad sleepers.

Table 1. Characteristics of birch wood samples treated by spent oils.

Wood samples	Amount of impregnant absorbed, A,%	Water absorption, B,%	Swelling after 30 days	
			Tangential, C_1,%	Radial, C_2,%
Natural birch wood	-	83.9	8.5	6.9
BW-ZHTK-2	59.8	26.9	7.3	6.9
BW-SEO	43.4	28.8	7.6	6.4
BW-STO	14.7	30.6	10.0	8.3
BW- SSO	43.6	35.2	12.7	6.4
BW-SCO	50.4	30.8	9.6	6.6

As follows from the table 1, the highest amount of the impregnating agent absorbed by wood phase was in case of ZHTK-2 (59.8%) and the lowest one for the sample BW-STO (14.7%), obviously, as a result of its higher viscosity. Water absorption ability of natural BW (83,9 %) decreased about 3 times when BW samplesimpregnated with ZHTK-2 and SEO, whereas other oils STO, SSO, and SCO provided 2.4-2.7 times lowering of water absorption.The swelling of the impregnated wood after 30 days ofcontact with distilled waterwas comparable both in tangential and radial directions for ZHTK and SEO (table 1). Taking into account that SEO is an industrial waste, possessing better properties comparing to ZHTK-2, the SEO was chosen as the basis of the impregnating composition (table 1).

The impregnating ability of wood is determined by the possibility of its wetting with an impregnating fluid. The first stage of wood impregnation goes via interfacial interaction of SEO with wood surface as a result of intermolecular interaction of their functional groups. The magnitude of wetting angle characterizes the degree of wetting of birch wood with engine oil. The values of wetting angle θ for birch samples treated by original motor oil (unused motor oil) was 47 ^{o}, while θ decreased to 31^o when wood samples impregnated by SEO. This fact is probably due to destruction and oxidation of hydrocarbon molecules of motor oil while operating the car engine. This resulted in formation of additional active groups in oil hydrocarbons molecules and the greater possibility of intermolecular interaction of SEO with functional groups wood.

In order to improve the quality of wood impregnation and increase its shape-stability, wood flour fillers (1 w. %) were introduced in to selected earlier SEO thus creating a number ofimpregnating compositions (table 2).

Table 2. Effect of wood flour from coniferous (WFC), hardwood (WFH), oak bark (FOB), birch bark (FBB) and pine bark (FPB) on characteristics of wood impregnation.

Impregnation composition	Amount of impregnant absorbed, A,%	Water absorption, B,%	Swelling after 30 days	
			Tangential, C_1,%	Radial, C_2,%
Natural birch wood	-	83.9	8.5	6.9
ZHTK-2	59.8	26.9	7.3	6.9
SEO	43.4	28.8	7.6	6.4
SEO+WFC	70.4	20.1	7.0	6.1
SEO+WFH	67.2	26.1	7.3	6.4
SEO+FOB	65.2	27.2	7.7	6.4
SEO+FBB	62.5	25.4	8.2	6.6
SEO+FPB	61.8	28.1	8.0	6.3

The introduction of wood flour into the used engine oil significantly increased the amount of the impregnating composition absorbed by wood, reduced water absorption, and slightly affected the swelling of wood in tangential and radial directions (table 2). The strongest effect on wood properties was observed for the SEO+WFC impregnating composition. In case of wood impregnation with ZHTK-2, the amount of impregnant absorbed was 10.4%higher than when treated with SEO+WFC composition.

Table 3 summarizes the effect of thefiller amount on dimensional stability and water absorption of wood samples.

Table 3. Effect of the amount of WFC filler of impregnating composition on properties of wood samples.

Impregnating composition	Amount of impregnant absorbed, A,%	Water absorption, B,%	Swelling after 30 days	
			Tangential, C_1,%	Radial, C_2,%
Natural birch wood	-	83.9	8.5	6.9
ZHTK-2	59.8	26.9	7.3	6.9
SEO	43.4	28.8	7.6	6.4
SEO + WFC 0.5%	47.8	35.6	8.2	6.3
SEO + WFC 1.0%	70.4	20.1	7.0	6.1
SEO + WFC 1.5%	54.2	31.8	7.9	6.6
SEO + WFC 2.0%	29.6	42.4	8.5	7.3

As follows from table 3, addition of WFC into impregnation composition cause an increase the content of impregnating material in wood, reduce wood water absorption and swelling in the tangential and radial directions. The strongest effect was observed when 1.0% of WFC was added to SEO. The role of WFC lies in enhancing the hydrophobizing effect of the impregnating composition as it contains abietic acid, soluble in SEO and acting as an hydrophobizing agent of wood. Physical indicators for specimens impregnated with developed impregnating composition (in comparison with ZHTK-2) were improved: the content of impregnating composition increased, water absorption decreased, swelling in tangential and radial directions decreased slightly (table 3).

It is well known that the impregnation ability of wood is a function of its wettability. The change of oil base of the impregnating composition from original engine oil (unused) to SEO led to a decrease of wetting angle of wood by 16°, thus, indicating better wetting of wood surface. The wetting angle decreased by 42° when processing wood with impregnating composition. As a result of oil oxidation during engine exploitation, destruction of SEO molecules occurred that was confirmed by a reduction of their molecule sizes from 490 nm (EO) to 35 nm (SEO).

The calculated values of kinematic viscosity of UEO (87.4 cSt) and SEO (41.2 cSt) confirmed the lower viscosity of SEO and its higher feasibility of using as the base for the impregnating composition.

Thus, the introduction of wood fillers into impregnation composition enhanced intermolecular interactions between components of the three-component system wood – SEO–filler of the developed impregnating formulation. Obviously, the product of intermolecular interaction in the system wood – SEO–filler was an additional obstacle for the release of oil from the wood phase.

4. Conclusion

An impregnation composition based on spent engine oil (99.0 w.%) and softwood flour (1.0 w. %) for treatment of birch wood to be used for railway sleepers manufacture was developed. In comparison to industrial oil antiseptic ZHTK-2, treatment of birch wood samples with elaborated impregnation composition caused a decrease of water absorption and swelling of wood samples.

The 14 times smaller diameter of hydrocarbon molecules in spent engine oil as compared to original engine oil resulted in lower viscosity and, thus, in better wood wetting and impregnation.

Softwood flour filler of the composition made an additional hydrophobizing effect on wood owing to abietic acid dissolution in spent engine oil and improvement of the intermolecular interaction of oil molecules and wood.

The developed composition is recommended for recycling of spent engine oils in wood based railroad sleepers production and substitution of concrete sleepers.

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