

Chromate-free Fixation of Copper by Hydrophobing

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Initial Situation and Objective

Timbers in soil contact or in direct contact with water must chemically be preserved against biological degradation by fungi and other microorganisms. The range of agents still permitted for that purpose is becoming smaller and smaller, as, due to European legislation, wood preserving agents must comply with the Biocides Directive, and as compounds that used to be very effective, such as creosotes and CCA salts, have been banned from that list meanwhile. Timbers in soil contact must be anticipated to be infested by organisms living in the ground that are capable of eroding various biocidal protection principles. Organic fungicides, for example, are degraded or copper is precipitated as an insoluble and thus ineffective copper oxalate. The most common wood-preserving agents for application in Hazard Classes 4 (in permanent contact with ground and fresh water) and 5 (installations in cooling towers, in permanent contact with sea water) have since been formulations with the biocide copper used with chromate as a fixation agent. The chromium(VI) and chromium(III) compounds, derived from the first, used for fixation, do not have any biocidal effect. However, the chromium(VI) compounds applied are highly toxic (carcinogenic and allergenic), so that possibilities of avoiding them, e.g., in hydrophobing are highly welcome.

The objective of the project was to work out a new concept to protect structural wooden parts in outdoor use exposed to leaching (Hazard Classes 2 to 4) with copper-containing agents combined with a hydrophobing feature based on drying oils. Contrary to the Royal procedure, hydrophobing in this respect was to penetrate into the inner parts of the timber, with the protective agent being introduced into the wood in the single-step process of empty-cell impregnation and cured there by means of microwaves.

Results

In the project under review, an oil recipe based on an isomerised soybean oil was developed that is fully curable on test samples of 10 mm x 10 mm x 50 mm, with or without a siccative, in an oxygen atmosphere after 17 to 24 hours. Furthermore, copper compounds in the form of copper soap were synthesised and introduced into the wood by way of the single-step impregnation procedure directly with the oil or also as an aqueous copper acetate solution by way of the two-step procedure before oil impregnation.

For copper placement sufficing Hazard Class 4, copper concentrations of 9 g/l to 13 g/l of oil were formulated. The storage stability of an isomerised oil mixed with copper octanoate was tested for a period of three months. Any notable polymerisation in the presence of Cu²⁺ in the form of the hydrophobic octanoate did not occur.

It could be shown that the distribution of copper in the wood across the entire cross-section of the sample was homogeneous (Fig. 1). Thereby, it had to be taken into account that the initially introduced quantity of the agent could reduce again due to empty-cell impregnation. It was noted that approx. only half (1.1 g/kg) of the originally introduced amount of copper (1.8 g/kg to 2.6 g/kg) remained in the wood after microwave treatment.

For accelerating the curing process, the test samples were stored in an oxygen atmosphere (p=10 bar) at an increased temperature (70 °C) for about 24 hours. This resulted in an almost complete decrease of the double compounds down into the interior of the timber in all cases, which was interpreted to be the result of almost complete curing.

The addition of a Co/Zr siccative had a heavily accelerating effect on the curing, while microwave treatment without a siccative did not lead to a faster decrease in

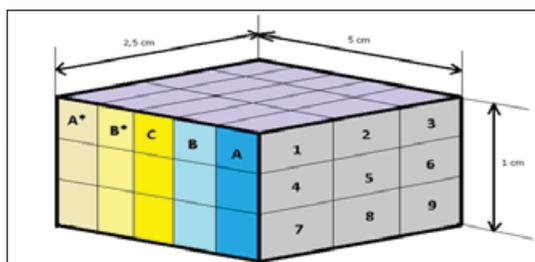
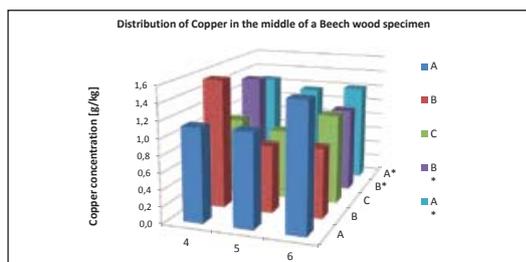


Fig. 1: Test sample completely soaked with copper octanoate/oil and treated with microwaves, split, individual samples dissolved by means of nitric microwave pulping, copper content investigated by MP-AES



the double compound. Copper octanoate itself has an additional siccative effect, which accelerates the networking reaction also by having the Co/Zr siccative to be added. In conjunction with the traditional siccative, however, it has a reaction-delaying effect.

In the presence of copper ions during the storage period, there was a slowly oxidative degradation effect in the oil in the samples previously looking well-cured. Increased mass loss was also noticed on the samples subjected to outdoor weathering after several months, due to sticky oil escaping from them.

This effect also had an impact on the leaching behaviour of copper, tested acc. to EN 84. In the two-week process, a delay in copper leaching was noted only when liquid, copper-containing oil had completely been removed from the wood. Then the oil-soluble copper octanoate, contrary to the variant hydrophobed by aqueous copper acetate, showed a lower leach rate than the chromate-fixed wood-preserving agent Korasit CC (Fig. 2).

Tests on the biological resistance towards the test fungi *Coniophora puteana* and *Trametes versicolor* showed fungus-impeding tendencies, with both variants with and without copper. So the mass loss, as contrasted to the virulence test, could be reduced in all variants by at least 50 %. Grading into HC 5 requires, however, a maximum mass loss of 3 %, which was achieved by only one variant (siccative oil) in the presence of *Trametes versicolor*. Especially notable was the large spread within the test group of oiled timbers, which was in no causal relationship with the batch treated with the agent. (Fig. 3).

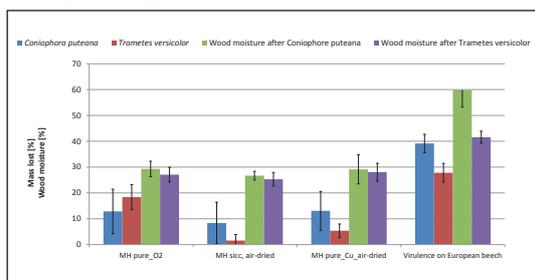


Fig. 2: Amount of copper in [%] leached from the initial amount contained in the wood after leaching (EN 84), mean values of $n^*=20$

One reason could be in the oil leach due to the liquefying process caused by copper, which resulted in the fact that the agent eventually remaining in the test sample did not unfold any significantly larger fungus-impeding effect than the hydrophobing effect due to the remaining oil. Analogue tendencies also showed

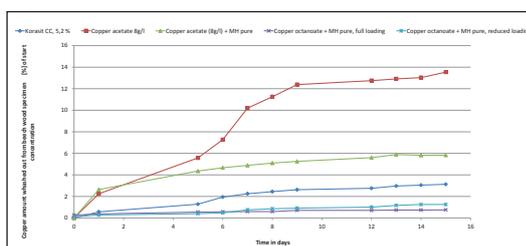


Fig. 3: Mass loss and wood moisture after EN 113 testing

in the resistance testing of soft rot, whereby, due to hydrophobing and in spite of the leaking of the copper-containing oil, the fungus-related mass loss could be reduced by 60%, too, as contrasted to natural beech.

Conclusion and Outlook

It can be summarised that the project goal, i.e., to achieve a reduction in copper leaching by hydrophobing, was met. Addition of copper to the oil had, despite complete initial curing, a liquefying effect on the oil, which eventually is counterproductive for the aspired use in HC 4 and HC 5. So, due to the remaining hydrophobing effects, better resistance towards fungi could be achieved, but, contrasted to the siccative variants without any agent, there was no further increase in these effects. A new approach consists in applying other leachable biocides, such as boron compounds or oils modified during application, which do not need to be cured oxidatively. First preliminary tests have already been performed and shall become part of a follow-up project that has already been applied for.