

# The chemistry of chromated copper arsenate II. Preservative-wood interactions

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**Abstract** The reactions which cause chromated copper arsenate preservative to fix strongly into wood are reviewed. A number of the mechanisms proposed in the literature appear chemically implausible. A new model is advanced in which the final fixation products are dominated by chromium (III) arsenate, chromium (III) hydroxide, and copper (II)- wood carboxylate complexes. Carboxylate groups should be generated in large numbers in the reduction of chromium (VI) by primary alcohol groups in lignin and carbohydrate fractions, or in the oxidative degradation of lignin. The model is supported by a recent X-ray absorption fine structure analysis.

## Introduction

Chromated copper arsenate wood preservative (CCA) exhibits broad spectrum toxicity based on the fungicidal properties of copper and the insecticidal properties of arsenic. Despite their bioavailability, in normal conditions the active components remain strongly fixed to the wood. Consequently CCA greatly increases the service life of timber exposed to weather, in ground contact, or even immersed in water. The precise chemical mechanism of fixation is of considerable interest in optimising fixation schedules, regulating use to avoid leaching, extracting the heavy metals from waste wood, understanding chemical loss during combustion, and designing future wood preservatives. Unfortunately the published chemical mechanisms of fixation are often speculative and even contradictory.

## Experimental

See Part I (Bull 2000).

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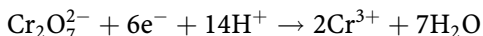
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## Results and discussion

The inorganic chemistry of CCA is driven by the reaction of chromate with wood:



Separated by the wood cell structure from the strong buffering action of bulk CCA solution, this consumption of hydrogen ions causes a significant increase in pH. Strongly insoluble chromium (III) arsenate will soon precipitate, since it rapidly polymerises at a critical pH of only 2.3, or less, at elevated temperature (Bull 2000). But since type I CCA typically has a Cr:Cu:As ratio of 2.0:0.9:1, there are simply not enough arsenates to complex all the Cr<sup>III</sup>. If fixation simply consisted of depositing sludge on the wood cell walls, over half the chromium and perhaps 80% of the copper would remain unfixed (Bull). Dahlgren and Hartford (1972a, b, c; Dahlgren 1974) recorded pH up to 5.5 in wood during CCA treatment, using a flat membrane glass electrode. Such low acidity could also precipitate copper (II) arsenates, and hydroxides, chromates, or carbonates of both metals.

Carbonates cannot be important fixation products since they are reasonably soluble, and CCA-treated wood exhibits minimal leaching to distilled water or dilute mineral acids. Chromates can be eliminated because Cr<sup>VI</sup> is definitely not present in fully fixed timber. This is usually demonstrated with a chromotropic acid spot test. Further, Kaldas and Cooper (1993) have presented Cr-2p XPS results showing complete conversion to Cr<sup>III</sup>. A number of authors have used electron spin resonance spectroscopy (ESR or EPR) to show that trace metastable Cr<sup>V</sup> intermediates can persist for up to six months (Ruddick et al. 1994; Hughes 1995). Cr<sup>V</sup> is a common intermediate in the reduction of Cr<sup>VI</sup> by organic species (Cotton and Wilkinson 1988). It is interesting that Cr<sup>IV</sup> is not observed, since the blue Cr<sup>IV</sup>O(O<sub>2</sub>)<sub>2</sub> is one intermediate in the room temperature reaction between hydrogen peroxide and acidified dichromate (Cotton and Wilkinson 1988). This may invalidate the comparison between fixation and peroxide reduction of CCA (Dahlgren and Hartford 1972c). On the other hand, Cr<sup>IV</sup> is an even stronger oxidant than Cr<sup>V</sup> and may simply decompose too quickly to be observed.

X-ray absorption fine structure spectroscopy (XAFS) of treated wood indicates that arsenate is predominantly bound to Cr, while Cu<sup>II</sup> is not closely associated with any other heavy element (Bull et al.). That is, there was no evidence for any significant amount of the copper (II) arsenates suggested by Dahlgren and Hartford (1972a). Thus, chromium (III) arsenate, chromium (III) hydroxide, and copper (II) hydroxide are the only plausible inorganic fixation products.

The metal cations might also fix onto any binding sites in the wood. Chemically speaking, wood is a highly structured composite of two polymers, lignin and cellulose, long chain heteropolysaccharides collectively called hemicellulose, and a wide array of derivatives and associated minor compounds. Cellulose and hemicellulose are grouped under the class of carbohydrates. There is a variety of possible linkages between the coniferyl alcohol monomers which make up lignin, resulting in a highly disordered network with a variety of functional groups.

Figure 1 shows the generalised structure for softwood lignin constructed by Adler (1977) which has the various substructures in approximately correct proportions.

Hughes (1995) has shown that both lignin and carbohydrates will reduce Cr<sup>VI</sup>. However, fixation is better on whole wood, which suggests that extractives are also involved. Wood does become slightly more brittle when treated, which is consistent with the removal or destruction of lubricant extractives. Cleavage of

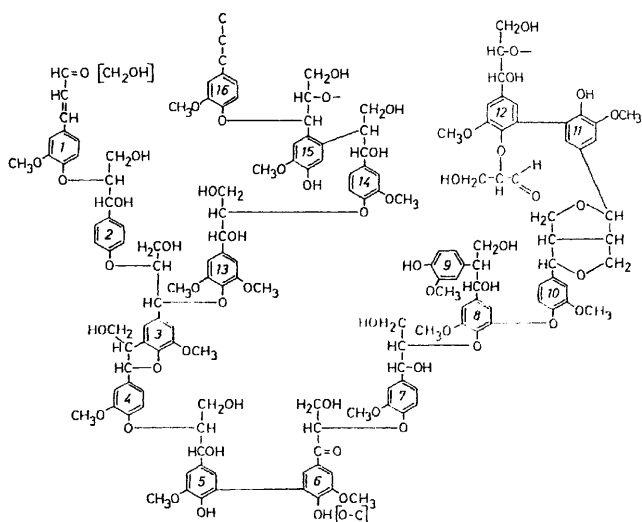


Fig. 1. Structure scheme for a general softwood lignin (Adler 1977)

polymer chains would result in a much greater loss of mechanical strength (Hartford 1986).

Ostmeyer et al. (1989) observed that CCA treatment caused a relative decrease in the part of the infrared spectrum due to aromatic ring vibrations. They proposed that chromic acid could form a stable ester with the aromatic rings of lignin (Fig. 2).

But the reaction is an oxidative attack, displacing two hydrogen ions. It should be written as in Fig. 3.

A  $\text{Cr}^{\text{IV}}$  product will certainly be unstable. More plausibly, abstraction of an electron from the hydroxy group will lead to a stable o-quinonoid, which might even oxidise further to a muconic acid structure (Fig. 4).

This reaction has been observed in the oxidation of guaiacol by permanganate or periodate (Adler and Magnusson 1959), and in the  $\text{ClO}_2$  stage of lignin bleaching. The standard potential for a related reaction, the reduction of benzoquinone to catechol, is only 0.7 V. That is substantially less than the standard chromate reduction potential of 1.35 V, so this reaction can be expected to proceed readily. Since benzoquinone has a peak in the relevant region of the infrared spectrum, but muconic acid does not (Pouchert 1985), the change in the infrared spectrum is probably due to cleavage of the aromatic rings.

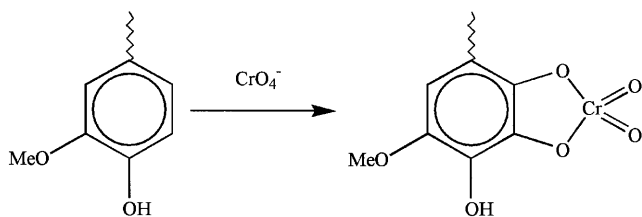


Fig. 2. Guaiacyl-chromate reaction proposed by Ostmeyer et al. (1989)

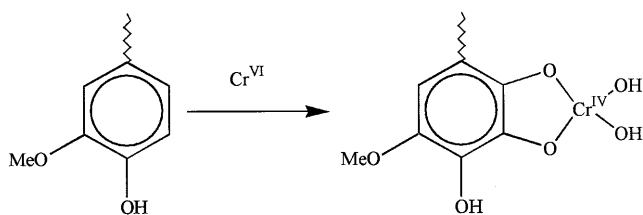


Fig. 3. Ostmeier et al.'s guaiacyl-chromate reaction revisited

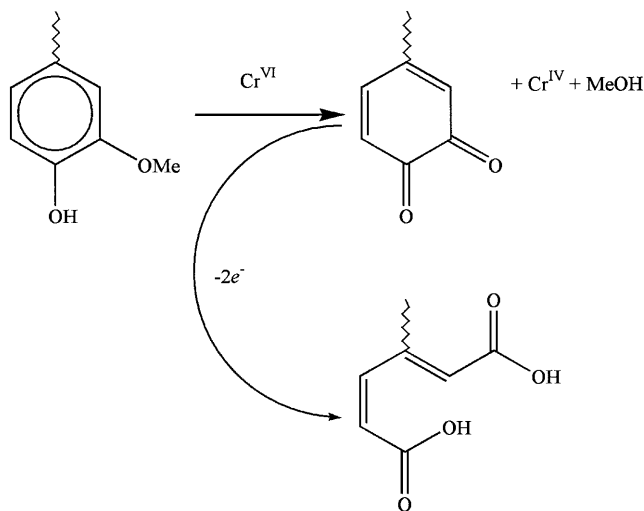


Fig. 4. Proposed guaiacyl-chromate reaction scheme

Permanganate, periodate, and  $\text{ClO}_2$  all proceed to attack the propyl part of the base unit, leading to depolymerisation and solubilisation of the lignin. Indeed, if the hydroxyl group is protected by methylation, the propyl chain is attacked preferentially (Adler and Magnusson 1959). However, since the physical properties of wood are not compromised by CCA treatment, either chromate is incapable of degradative oxidation under these conditions, or the reaction does not reach that point in practice.

In an attempt to support the chromic ester hypothesis of Ostmeier et al., Pizzi (1990) reacted guaiacol with chromate and analysed the resulting precipitate by  $^{13}\text{C}$ -NMR, obtaining the spectrum reproduced in Fig. 5.

He concluded that the shift of the 6-carbon signal from its usual place at around 110 ppm was due to the formation of the chromic ester. But the spectrum as a whole is more consistent with partial conversion to muconic acid, which explains the substantial peak that has appeared at around 200 ppm.

Pizzi carried out molecular modelling calculations optimizing non-bonded interactions, and proposed three further types of chromium-lignin complexes on that basis (Fig. 6).

Pizzi's type 2 and 4 complexes can be eliminated out of hand. As written, the type 2 complex involves  $\text{Cr}^{\text{VII}}$ . Since this is quite impossible, one of the oxo donors should probably be rewritten as a hydroxo group. But that still gives

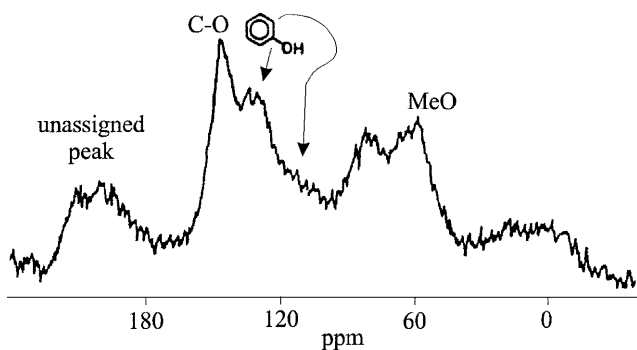


Fig. 5.  $^{13}\text{C}$  NMR of guaiacol-chromate reaction product (Pizzi 1990)

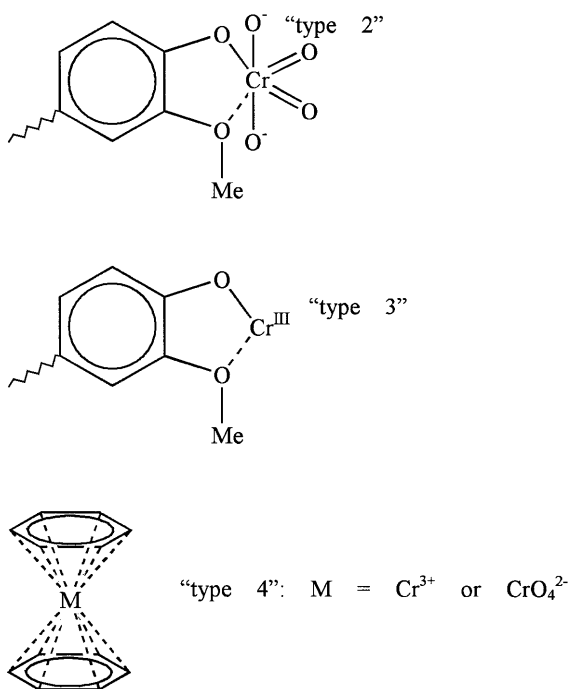


Fig. 6. Cr-wood interactions proposed by Pizzi (1990)

6-coordinate  $\text{Cr}^{\text{VI}}$ , which is equally implausible. In any case, like the type 4  $\text{Cr}^{\text{VI}}$  complex, it requires an anion to be attracted to a  $\delta$ -negative region of the molecule; Pizzi's calculations appear inconsistent with elementary electrostatic considerations.

Pizzi's claim that the type 4  $\text{Cr}^{\text{III}}$  complex is similar to ferrocene is not readily apparent. Ferrocene is bis(cyclopentadienyl)iron (II). The aromatic radical anions are stabilised by donation from the  $\pi$  system into the valence shell of the cation. The 18 electrons, six  $\pi$  from each ring and six 3d from the metal, neatly fill the 9 bonding orbitals. There is no such mutual advantage in the 15-electron system of  $d^3$   $\text{Cr}^{\text{III}}$  and two  $6\pi$  substituted benzenes. Dibenzenechromium (0) does obey the

18-electron rule, but it cannot form in these conditions, nor is it stable toward aromatic substitution.

The type 3 interaction, coordination of  $\text{Cr}^{\text{III}}$  to a phenolate, is much more sensible. However, the  $\text{pK}_a$  of phenols is substantially higher than that of carboxylic acids, making it relatively difficult for metals to displace hydrogen ion at low pH. While basic copper preservatives appear to bind to phenolates, this is unlikely in acid preservatives like CCA (Hughes 1995).

Carboxylate residues could easily complex metal ions at these acidities. There are some carboxylate residues in hemicellulose, and the muconic acid hypothesised earlier is a carboxylic acid. But a better source is the primary alcohol groups, which will readily react with  $\text{Cr}^{\text{VI}}$  to give carboxylic acids. Primary alcohols are plentiful in both lignin (Fig. 1) and carbohydrates. They must be terminal to chains, therefore relatively accessible. It also follows that their oxidation does not change the backbone of the chain significantly.

Ostmeyer et al. (1988) also suggested that  $\text{Cr}^{\text{VI}}$  might oxidise propenyl chains in the lignin, presumably yielding a secondary alcohol. However, double bonds are relatively rare in softwood lignin (Fig. 1) and slightly less accessible than primary alcohols. While this reaction appears quite feasible, it is unlikely to contribute much to fixation.

A number of workers (Ostmeyer et al. 1988; Kaldas and Cooper 1993; Ruddick et al. 1993) have attempted to use X-ray photoelectron spectroscopy (XPS) to observe chemical changes of the wood during fixation. XPS carbon-1s spectra show separable peaks for carbon-containing groups, depending on the number of carbon-oxygen bonds (Fig. 7), so it was thought that the technique would shed some light on the oxidation of wood by  $\text{Cr}^{\text{VI}}$ , and therefore on the fixation products.

Unfortunately, the results have been very inconsistent, and the reported C1:C2 ratios are generally much higher than would be expected. Ruddick et al. (1993) hypothesised that migration of C1- rich extractives toward the surface of the wood during soaking and drying compromises XPS analysis. The sampling depth

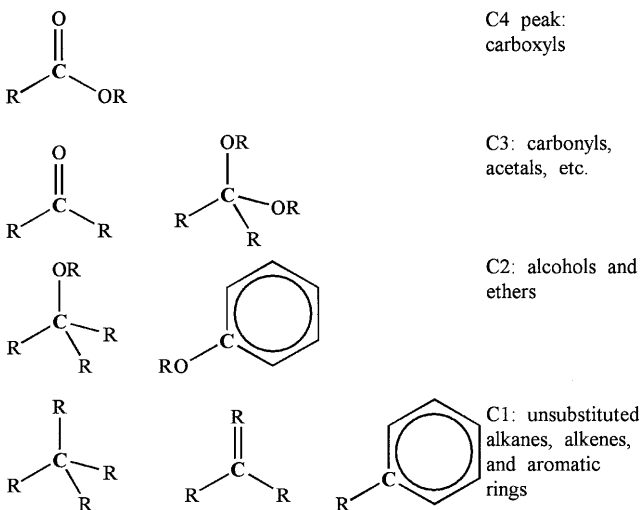


Fig. 7. Differentiation of functional groups by C1s XPS

for XPS is only a few nanometres, which makes the technique extremely vulnerable to surface effects.

Kaldas and Cooper (1993) observed a massive drop in C4 peak area, indicating loss of carboxyl groups through acid-catalysed decarboxylation. However, this is unlikely to occur in practice. Their exposure of thin wood slices to a vast excess of bulk CCA must have maintained solution acidity at a much higher level than normal.

The experiments of Pizzi et al. (1984) to determine distribution of preservative on lignin or holocellulose fractions are not helpful in determining the nature of the fixation products. The reagents used to separate the fractions appear to include strong sulfuric acid, which will certainly dissolve any purely inorganic CCA fixation products, and probably break up any wood-metal ion complexes too (Honda et al. 1991). Therefore, the results cannot be representative. Since wood is a closely linked copolymer, with some bonding between the carbohydrate and lignin, even the concept of distribution does not seem particularly useful.

Since ligand exchange reactions of Cr<sup>III</sup> are extremely slow, it will have difficulty in binding to carboxylates even at apparently favourable pH. On the other hand, its precipitation as the hydroxide will be relatively rapid at sufficiently low acidity. Consequently, the binding sites will be readily available to Cu<sup>II</sup>. It is therefore proposed that *the fixation products of CCA are dominated by chromium (III) arsenate, chromium (III) hydroxide, and wood carboxylate-copper (II) complexes.*

This separation of Cu from Cr and As is consistent with the observation that acetic acid, humic acid, EDTA, and liginosulfonic acid could all extract the majority of the Cu from treated wood, yet leave most of the Cr and As (Kazi and Cooper 1998). Conversely, oxalic acid extracted only 55% of the Cu, but almost all of the Cr and As. Similarly, Fox et al. (1987) observed that the leachability of Cu from treated wood increased with decreasing pH, whereas Cr and As were not significantly affected. Pasek and McIntyre (1993) were able to extract a considerable proportion of the Cu from CCA-contaminated soil using NH<sub>3</sub> solution. Ruddick (1992) reported selective leaching of Cu from treated wood in field tests, possibly due to bacterial action.

## Conclusion

This model is substantially simpler than those proposed by Pizzi or by Dahlgren and Hartford. Nonetheless, it is capable of explaining all the spectroscopic observations and a number of empirical results. Further, it is more consistent with known chemistry.

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