Wood Waterproofing and Lignin Crosslinking by Means of Chromium Trioxide/Guajacyl Units Complexes

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Synopsis

A CrO_3/guajacyl polymeric complex was prepared and characterized. The increased crosslinking of the lignin network in wood afforded by the equivalent CrO_3/guajacyl units complexes as well as the insolubility of these complexes are the cause of the enhanced water resistance presented by the CrO_3-treated wood. Chromium trioxide was found to be the complexing species. Chromium (VI) was not reduced to chromium (III) during the treatment. A parallel with the lignosulfonates/dichromate gel formation was made.

INTRODUCTION

Wood preservation by treatment with chromium salts, such as copper chromium arsenates, is fast gaining wider industrial acceptance than more traditional, though still effective, systems of preservation, such as creosoting. In more recent developments, wood impregnation by chromium trioxide solutions has been reported to considerably improve swelling, water resistance, and water repellancy of the treated wood.[1-3] Furthermore, the treatment of wood with chromium trioxide gives results superior to those obtained with chromium salts such as copper chromium arsenate. The waterproofing effect of CrO_3 appears to be of a different nature than that induced by copper chromium arsenates. In this context, different Cr(VI) salts have also been reported to have a similar effect though to a much lesser extent.[4]

However, these salts have been shown to release, under cold and boiling water extraction of the treated wood, considerably higher amounts of chromium.[4] This phenomenon, which indicates only partial fixation of the salt on the wood structural constituents, has been observed only to a minimal extent in the case of the chromium trioxide treatment. Definite hypothesis on the possible role of CrO_3 or of Cr (VI) in this context have not been advanced. It is not known if (1) chromium is attached to cellulose or to lignin and (2) if it is attached in the form of Cr (VI) or is instead reduced to Cr (III) before being fixed to one or more of the structural components of wood. The bonds formed appear to be of a chemical nature as prolonged extraction of the treated wood with boiling water did not, in the case of CrO_3 with heat treatment, yield substantial quantities of chromium in solution.[4]

However, it would appear that the action of the chromium trioxide is confined to the formation of complexes with the lignin of the wood rather than with cellulose.

Chromium trioxide is soluble in water forming a yellow solution of chromic acid.

$$CrO_3 + H_2O \rightarrow 2H^+ + CrO_4^=$$
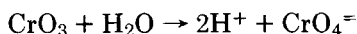
In more concentrated solutions, orange-colored dichromic acid is formed

$$2CrO_3 + H_2O \rightarrow 2H^+ + Cr_2O_7^=$$

A reaction analogous to wood preservation by means of CrO_3 impregnation may be found in the treatment of spent sulfite pulping liquors with dichromate ions which effect gel-like structures.[5] Considerable speculation has been taking place about these chromic complexes with lignosulfonates.[5] The lignosulfonate molecular weight increases about twentyfold as a consequence of the dichromate treatment. The possibility that the molecular weight increases are due to aldehyde–phenol condensation reactions (alifatic methylol groups are present in lignosulfonates) was discounted by the low reactivity of formaldehyde with sodium lignosulfonate under gel-forming conditions.[5] Recent developments[6] on the formation of phenols/formaldehyde Cr (III) complexes and on their influence on the phenol–aldehyde reactions do not allow hasty discarding of this idea, though considering the relative positions to the aromatic rings of the methylol groups in lignosulfonates the possibility of formation of such complexes is indeed remote.

The crosslinking could of course originate from oxidative phenoxy coupling reactions described earlier and Hayashi and Goring[7] have pointed out that reactions between dichromate and catechol are similar to those of the dichromate–lignosulfonate system. Slabbert[8] has shown that chromium as well as other metallic ions are capable of forming stable chelates with o-hydroxyphenol nuclei bound to the metal varying according to the metal used, its valence state, and the pH of the solution.
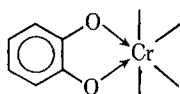
This article aims at clarifying, by using very unsophisticated model compounds, the nature of the complexes formed during waterproofing treatment of wood with chromium trioxide, which of the wood constituents form these complexes, the valence state of the chromium, and the reason for the waterproofing effect observed. As an approach, guajacol (o-methoxyphenol) was used as a simple model to imitate the abundant guajacyl units of lignin. Glucose was used as a model compound for cellulose. Chromium (VI) was used only in the form of chromium trioxide. Notwithstanding the oversimplified models chosen, interesting results were nonetheless obtained. Contact of dilute chromium-trioxide solutions and guajacol afforded instantaneous precipitation of a dark purple–brown polymeric complex insoluble in water. Glucose, conversely, did not form insoluble complexes with chromium trioxide. The waterproofing action of the chromium appears then to be confined to the formation of insoluble water-repellent complexes with the lignin in wood.

EXPERIMENTAL

Guajacol

When guajacol was added to aqueous solutions of chromium trioxide, a complex precipitated immediately. To control the reaction and avoid precipitation at ambient temperature, very diluted solutions were used; to 25 mg of guajacol in 10 ml of water were added 5 mg of chromium trioxide in 40 ml of water. The solution was clear and passed from the bright yellow color characteristic of chromic acid to a dark brown–purple color as soon as mixing was completed. The solution was then refluxed for 30 min and a dark purple–brown precipitate formed. The suspension was centrifuged for 3 min and then the liquid decanted and stored. The dark purple precipitate was washed in water and then centrifuged again. The procedure was repeated three times. The precipitate was then dried under vacuum in a rotary evaporator (600 mm Hg, 50°C). The reaction was repeated several times in order to obtain several samples. Different tests were performed on the dark purple–brown compound, many of them indicating it to be an amorphous polymer.

Mass Spectra

Mass spectra of the compound were made using a Hewlett–Packard quadrupole electrical mass spectrometer. Compounds of MW = ±800–1000 were present but the m/e of the peaks in question varied continuously over the 10 min bisecondwise scanning, indicating that the material was a complex polymeric material. The largest and most consistent m/e fragments of such polymer (M+ 466) had the fragmentation pattern shown in Figure 1.
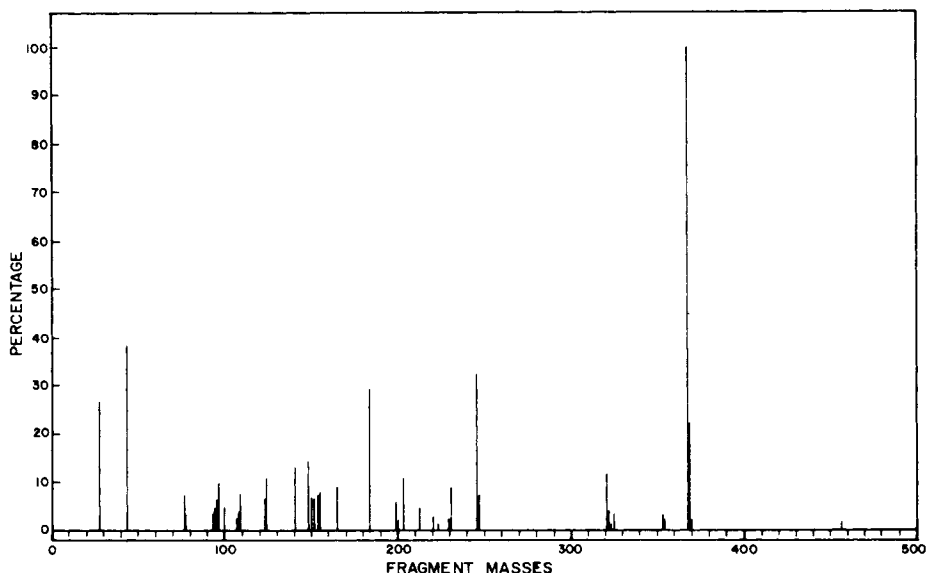

Fig. 1. Mass spectrum of major fraction of polymeric CrO_3/guajacol complex.

Infrared Spectra

Pills of 6‰ of the material in KBr were analyzed by infrared spectrometry. The peaks of the spectra were broadened both for the presence of the bound metal ion and for the polymeric nature of the material. A broad —OH band, in comparison with pure guajacol, indicated an —OH intermolecularly bound, perhaps with chromium: 3800–2700, peak 3400 cm^{-1}, (—OH), 1670 cm^{-1}, 1590 cm^{-1}, 1510 cm^{-1}, 1510 cm^{-1}, 1480 cm^{-1}, 1460 cm^{-1}, 1390 cm^{-1}, 1260 cm^{-1}, 1210 cm^{-1}, 1120 cm^{-1}, 1030 cm^{-1}, 920 cm^{-1} (small) 840 cm^{-1}, 810 cm^{-1} (all broad bands). Guajacol, pure = 3600–3200, peaks 3500 and 3450 cm^{-1}, 3050, 3000, 2950, 2850, 1610, 1595, 1500, 1470, 1440, 1380, 1300, 1260, 1220, 1170, 1150 (small), 1105, 1040, 1020, 915, 830, 740 cm^{-1} (strong), all sharp bands.

ANAL. Experimental: C, 36.17%; H, 4.63%; O, 36.00%; N, 0.30%. Calcd: C, 38.61%; H, 3.14%; O, 35.89%.

Atomic Absorption Spectra

Chromium content: calcd = 23.3%; experimental = 22.1%.

X-Ray Diffraction

No patterns obtained; material completely amorphous.

The melting point was > 300°C. Part of the stored liquid was also dried on a rotary evaporator and the residue underwent similar examination as those described for the solid. The mass spectra showed that m/e 446 was also the fragment of higher consistent mass and that the fragmentation pattern obtained was just about identical to that already presented for the solid. Part of the liquid underwent UV examination to ascertain if more than one metal/ligand ratio, indicating equilibrium of more than one complex, was present.

UV Spectra

The only maximum of absorption was found at 531 nm; spectra of the solutions at pH 2.2, 3.0, 4.3, 5.0, 7.4, 9.1, 9.9 were done. The absorbance curve, at 531 nm fixed, in function of the pH indicated that of only one metal/ligand ratio,[9–11] hence only one type of complex, is present and that complex is relatively stable in the approximate pH range 2.2–7.4 and most stable in the pH range 4.3–7.4. The absorbance ratio of different pH/pH 5 was pH 2.2 = 0.35; pH 3.0 = 0.96; pH 4.3 = 0.98; pH 5.0 = 1; pH 6.2 = 1.0; pH 7.4 = 1.0; pH 9.1 = 1.55; pH 9.3 = 2.45; using 300 mg. The reaction was repeated using 300 mg guajacol and 5 mg chromium trioxide in 50 ml of water. After 30 min reflux, only light traces of olive-green precipitate was noticed.

Glucose

No insoluble reaction products of glucose and chromium trioxide were found under the same molar proportions, concentrations, and reaction conditions used for the guajacol–CrO$_3$ reaction.

Wood

Small, finely and freshly cut specimens of Pine (*Pinus patula*) were immersed at ambient temperature in a diluted solution of chromium trioxide. Dark-purple spots started to appear on the surface of the wood corresponding to the wood rays, then the whole piece of wood became light olive green in color, and then, at the end, first dark purple and finally dark brown.

The experiments were repeated using solutions of chromium sulfate and chromium acetate. Complexes were formed but all of them were soluble in water.

DISCUSSION

Chromium trioxide is capable of forming insoluble complexes with guajacol, and by analogy, with the guajacyl units of lignin (guajacyl units constitute 80–90% of the aromatics in lignin). The results obtained from the mass spectra show that the insoluble amorphous Cr (VI)/guajacol complex is in polymeric form as more than traces of variable mass fragments m/e 800–1000 are present. The highest mass consistent fragment is m/e 446. This indicates only two possibilities for the complex structure:

$$[\text{guajacol}]_2 \cdot [\text{Cr}]_2 \cdot [\text{phenol}], \tag{1}$$
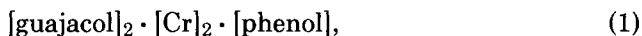
where the phenol is just the residue of a demethoxylated guajacyl unit and the chromium is in its trivalent form or

$$[\text{guajacol}]_2 \cdot [\text{CrO}_3]_2 \tag{2}$$
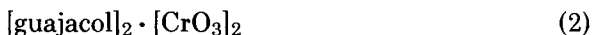
in which the complexing species is not chromium but chromium trioxide and the Cr is in its exavalent form. The results of the elemental analysis indicate clearly that complex (2) is the one formed. The mass-spectra fragmentation pattern, as well as the atomic absorption values for the chromium content, confirms this fact. This indicates that Cr (VI) is not reduced to Cr (III) during the formation of complexes with guajacol and, by inference, with lignin.

IR and UV spectra show that the chromium is definitely chemically bound to the guajacol. In particular, the UV variable pH/pH 5 ratio interpretation according to Job's,[9] molar ratio,[10] and slope ratio[11] methods indicate that the Cr (VI):ligand ratio is definitely and only 1:1 and that there is no equilibrium with other complex species. In the IR spectra, a much broader —OH band than in the case of pure guajacol indicates that the —OH is intermolecularly bonded. This may indicate a variety of possibilities, namely that (1) CrO3 is bound to the phenolic —OH of the guajacyl residues, or that (2) a molecule of water is linking, intramolecularly, Cr (VI) and the guajacol —OH, though this possibility is unlikely, or that (3) guajacyl residues are linked together by phenoxy-coupling created during the reaction with Cr. Both the first and the last possibilities are highly likely. Guajacol phenoxy-coupling is strongly indicated by the mass of spectra-abundant m/e 369, 368 (three-coupled guajacyl units), (residues of bigger fragments), and m/e 246 (two-coupled guajacyl residues). The general broadening of all the guajacol IR bands, once complexed with CrO3, is an indication of the presence of a heavy atom [Cr (VI)] bound to the guajacol, as well as of the polymeric nature of the material.

By comparison of complexes formed by chromium (III) and catechol (I)[7,8] a

structurally similar type of complex for CrO_3 and guajacol, in which the two CrO_3 may or may not be linked, can be visualized. However, given the polymeric nature of the material, it is doubtful that the same CrO_3 is bound to the oxygens of both hydroxy and methoxy groups of the same guajacyl residues as proposed by Hayashi and Goring[5,7] for dichromate–lignin complexes; it is difficult to visualize how such a complex could then be in polymeric form. The polymeric nature of the material and the proposed formation of five-term-ring complexes similar to those formed by metals with o-hydroxyphenols[8] can be reconciled by visualizing a continuous tridimensional network of CrO_3 in which every oxygen is shared by two chromium atoms with guajacyl units coordinated to the chromium by hydroxy and methoxy groups oxygens to form a five-term-ring including the metal. Conversely, a linear polymer composed by alternating guajacyl and CrO_3 units can be visualized.

Glucose did not form any insoluble complexes with CrO_3, indicating that cellulose does not participate actively in the waterproofing mechanism. Previous authors[12] have reported the formation of Cr (III)-containing precipitates by reaction of glucose with copper chromium arsenates. The formation of such complexes in the case of copper chromium arsenates is undeniable and is due to the reducing effect of glucose on the chromium salt. In the case of copper chromium arsenates, precipitation starts, at 100°C after 25–40 hr and at 40°C after 600–1500 hr according to the type of copper chromium arsenate treating mixture used.[12] In the case of the CrO_3 treatment, the situation is completely different as fixation to the wood of the chromium complexing species is completed at 100°C in no more than 30 min and at ambient temperature in no more than 170 hr.[4] This indicates that the much slower glucose reduction effect does not play an important role in the case of the CrO_3 treatment. Latter work[13] has also shown that only in considerably more diluted solutions than those used in wood treatment practice a small amount of Cr (VI) is reduced to Cr (III), indicating that the cellulose, hence the glucose, reducing effect is indeed negligible. At higher concentration such an effect has not been observed.[13]

Chromium (III) salts do not form insoluble complexes with guajacol, confirming again that the waterproofing effect is due to Cr (VI). The fact that Cr (III) forms complexes with lignin and lignosulfonates is certain,[14] though such compounds are more likely to be inter- and intramolecular complexes of Cr (III) with both the methylol and phenolic hydroxy groups of lignin, similar in nature to phenols–formaldehyde–Cr (III) soluble complexes already described.[6] From what is described, it appears that wood waterproofing by CrO_3 treatment[1–3] and the macrogel formation by reaction of lignin or lignosulfonates with dichromate ions[5,7,14] are indeed related reactions. The picture of the lignin–dichromate gel which has been speculated,[5,14] namely of a condensed lignin or lignosulfonate containing carboxyl groups, and coordinated to hydroxylated chromium ion species by all types of its acid functions may well be incorrect. From the CrO_3–guajacol complexes it appears that acid groups are not necessary to the formation of the insoluble complex.

The wood waterproofing effect that CrO_3 presents does then appear to be due to a considerable increase in lignin crosslinking, through CrO_3 bridges, hence an increase in the lignin network strength and stability, counteracting the cellulose tendency to swell by absorbing water. Furthermore, the more highly crosslinked lignin network will render it more difficult for the water to reach the

cellulose, with decreased swelling.   Last but not least, the insolubility of the CrO_3–guajacol complex indicates that CrO_3–lignin complexes are also insoluble, indicating a high degree of water repellency that contributes to the wood waterproofing.

The progression of colors in the wood within one week of ambient temperature treatment (wet–dry) strongly indicated that a parallel exists between what happens in the wood and the formation of the CrO_3–guajacol complexes.

CONCLUSIONS

Wood is apparently waterproofed and lignin and its derivatives are crosslinked by formation of chromium (IV)–guajacyl units complexes.   The consequent increased crosslinking of the lignin network obtained, as well as the insolubility of the complexes formed, are the probable causes of the enhanced water resistance and water repellency acquired by the wood after the treatment.

Chromium trioxide is the complexing species and the structure of the polymeric complex formed can be given as

$$\left[\left[\underset{2}{\overset{\text{OH}}{\bigcirc}}\text{OCH}_3 \right] \cdot [CrO_3]_2 \right]_n$$
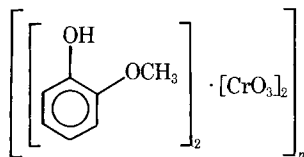
with $n \geq 2$.   Chromium (VI) is not reduced to chromium (III) during the reaction with guajacyl units.

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