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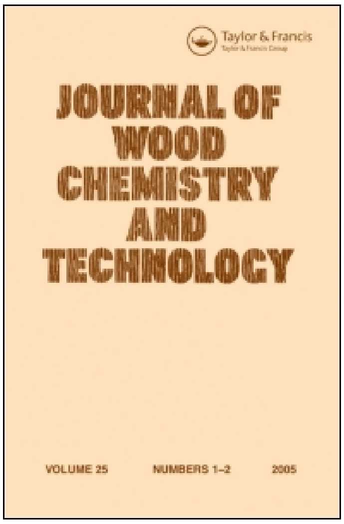

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Protection of Wood Surfaces with Metallic Oxides

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PROTECTION OF WOOD SURFACES WITH METALLIC OXIDES

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ABSTRACT

Zinc oxide as well as lead (II), lead (IV) and tin (II) oxide have been found to react with guaiacol as a simple lignin model compoun to form complexes. In comparison with results obtained with chromium trioxide, only zinc oxide is able to give worthwhile results when used to waterproof wood. Because of the "dimeric" character of the complex formed with lignin, zinc oxide is a less efficient wood waterproofer than CrO_3, which instead forms "polymeric" complexes. A theory of the preservation effect of wood by metallic ion is advanced. The results obtained indicate that metallic compounds which are capable of further cross-linking the lignin network by forming insoluble complexes with it can act as wood waterproofers. Metallic compounds giving insoluble monomeric complexes not enhancing lignin cross-linking or not giving insoluble complexes do not act as wood waterproofer.

INTRODUCTION

Many beneficial properties can be imparted to wood surfaces by treatment with aqueous solutions of certain inorganic chemicals[1]. Amongst them chromium trioxide solutions have been found especially effective for improvement of swelling, water resistance and water repellency of wood[1-5]. The effect of chromium trioxide has been ascribed to the formation of insoluble complexes between the oxide and the guaiacol units of lignin[5].

This paper is aimed to determine the improvement in water resistance and water repellency of wood surfaces after treatment with metallic oxides of hydroxides other than chromium. The first stage of this study is concerned with reactions between guaiacol as a simple model compound of lignin with metallic oxides to form insoluble complexes. In the second stage, the effect of oxides forming insoluble complexes has been tested.

EXPERIMENTAL

Chemical Reactions

Reactions of guaiacol with different metallic oxides - As(III), Fe(III), Cu(II), Pb(IV), Mg, Mn(II), Zn and Sn(II) - in acidic solution

Between 1 and $10 \cdot 10^{-3}$ mol of the respective oxide was dissolved in hydrochloric acid (32 %) (6 % HCl for ZnO). To this solution was added double the equimolar amount of guaiacol. After one hour, the solution was neutralized with sodium hydroxide solution and any precipitate formed, was filtered and washed with water and methanol. In the case of PbO_2, the reaction mixture was cooked for one hour after neutralizing. Precipitates were dried in a desiccator. Results are shown in Table 1.

Metallic oxide - guaiacol complexes formed:

Lead-guaiacol complex

Yield: 83%

I.R.-KBr(cm^{-1}): 3300-3600(*w*)*, 3050, 3010, 2930, 2830, (all *m*), 1580, 1475, 1440, (all *s*), 1330(*m*), 1270, 1240, 1210, 1170, 1105, (all *s*), 1040(*m*), 1020(*s*), 905(*w*), 840, 750, 730, (all *s*), 585(*m*), 350-450(*m*).

* Intensity: *w* = weak, *m* = medium, *s* = strong

TABLE 1
Results of Reactions Between Guaiacol and Metallic Oxides

Oxide	Solvent	Precipitate with guaiacol/colour	Comments
ZnO	dil. HCl (6%)	yes/colourless m.p. > 300 ^{o}C	reaction time 24 hours; when cooked before neutralizing, white inorganic precipitate
ZnO	methanol/H_2O (2:1)	yes/colourless m.p. > 300 ^{o}C	
$Zn(OH)_2$	H_2O	yes/colourless m.p. > 300 ^{o}C	
As_2O_3	conc. HCl	no	
Fe_2O_3	concl HCl	no	
CuO	conc. HCl	no	brown inorganic precipitate
PbO	conc. NaOH (25%)	yes/colourless m.p. > 300 ^{o}C	after neutralizing, one hour cooking
PbO_2	conc. HCl	yes/colourless m.p. > 300 ^{o}C	after neutralizing, one hour cooking
MgO	conc. HCl	no	
MnO_2	conc. HCl	no	
CrO_3	-	yes	darker purple - brown
OsO_4	H_2O	no	black inorganic precipitate
Ag_2O	conc. NH_3 sol. (25%)	no	brown inorganic precipitate
SnO	conc. HCl	yes/light yellow m.p. > 300 ^{o}C	when cooked before neutralizing, white inorganic precipitate

Elemental Analysis: Found C = 25.45%; H = 2.09%

Calculated C = 25.47%; H = 2.14%

Zinc-guaiacol complex

Yield: 77% (only partly - 94% - reacted)

For analytical data see below.

Tin-guaiacol complex

Undefinable composition (compare discussion)

I.R.-KBr(cm^{-1}): 3300-3600(*m*), 3060, 2940, 2840, (all *w*), 1585(*m*), 1485(*s*), 1450(*m*), 1330(*w*), 1270(*m*), 1245(*s*), 1205, 1170, 1105, 1040, 1020, (all *m*), 910(*w*), 840, 750, 735, 400-650 (all *m*).

Elemental Analysis: Found C = 12.22%; H = 1.26%

Reaction of guaiacol with lead(II) oxide

Lead(II) oxide Mezck laboratory reagent grade (2.23 g, 10^{-2} mol) was dissolved in 25% sodium hydroxide solution and guaiacol (2.48 g, 2·10^{-2} mol) was added. After one hour stirring, the solution was neutralized with HCl and cooked for one hour. The precipitate formed was filtered, washed with water and methanol and dried in a desiccator - compare Table 1.

Lead-guaiacol complex

Yield: 57%

I.R.-KBr: equal to that above.

Elemental Analysis: Found C = 27.15%; H = 2.20%

Calculated C = 25.47%; H = 2.14%

Reaction of guaiacol with osmic tetroxide

Osmic tetroxide (100 mg, 3.9·10^{-3} mol) was dissolved in 20 ml water and guaiacol (99 mg, 8·10^{-3} mol) was added. The solution became brown in colour and a precipitate was formed. After 24 hours reaction time, the dark brown inorganic precipitate was centrifuged and washed with water and chloroform - compare Table 1.

Reaction of guaiacol with silver oxide (AG_2O)

Silver oxide BDH laboratory reagent grade, (1.16 g, $5 \cdot 10^{-3}$ mol) was dissolved in 25% ammonia solution and guaiacol (1.24 g, 10^{-2} mol) was added. After one hour the solution was neutralized with HCl. No precipitate was formed - compare Table 1.

Zinc-guaiacol complex without use of acid

To a solution of guaiacol (3.10 g, $2.4 \cdot 10^{-2}$ mol) in 25 ml methanol/water (2 : 1) zinc oxide (0.51 g, $6 \cdot 10^{-3}$ mol) was added. The suspension was stirred for six days. Then the precipitate was filtered and washed three times with water and twice with methanol, and dried in a desiccator.

Yield: 59%

I.R.-KBr(cm^{-1}): 3300-3600(*w*), 3060, 3000, 2970, 2930, 2830, (all *m*), 1580, 1480, 1445, 1315, 1280, 1245, 1200, 1165, 1100, (all *s*), 1030(*m*), 1015(*s*), 910(*m*), 840, 750, 730, 585, (all *s*), 565, 530, 460, 435, (all *m*).

Elemental Analysis:			
	Found	C = 53.93%;	H = 4.44%
	Calculated	C = 53.95%;	H = 4.54%

Zn (OH) complex[6]

This was prepared according to the method of Anzai et al[6]. Yields and analytical data were in agreement with those already reported[6].

Applied Work on Wood

Test specimens of South African pine (*Pinus patula*) and European beech (*Fagus sylvatica*) were used in this study. Specimen sizes were 25 mm x 25 mm x 50 mm (radial x tangential x longitudinal). For each experiment two specimens were used. The solutions used were:

- zinc oxide: 405 mg/500 ml H_2O (10^{-2}mol/l)
- zinc oxide: 4.05 g/500 ml H_2O (10^{-1} mol/l) + 10 ml conc. HCl
- zinc hydroxide: 447 mg/500 ml H_2O (10^{-2} mol/l)
- chromium trioxide: 5.00 g/500 ml H_2O (10^{-1} mol/l)
- chromium trioxide: 500 mg/500 ml H_2O (10^{-2} mol/l)

The metallic oxide (or hydroxide) water (or acidic water) solution was placed in a glass beaker. Then after measurement of their dimensions and masses at 25°C and 12% e.m.c., the wood specimens were immersed in those solutions for five days. The acidic solution was neutralized and allowed to stand for five additional days. After treatment, the wood specimens were dried for 24 hours at about 50°C. After conditioning at 12 % e.m.c., the test specimens were tested for their water repellency by measuring a drop of water contact or wetting angle on the surface of the treated wood at a temperature of 25 °C - compare Figures 1 and 2.

For the measurement of thickness swelling and water absorption, the treated wood specimens and untreated specimens were soaked in water. At fixed times, masses and radial and tangential dimensions of the specimens after water soaking were measured. The average values were used, respectively, for calculating the variation of the percentage water absorption and the percentage swelling after water soaking - compare Figures 3 to 6.

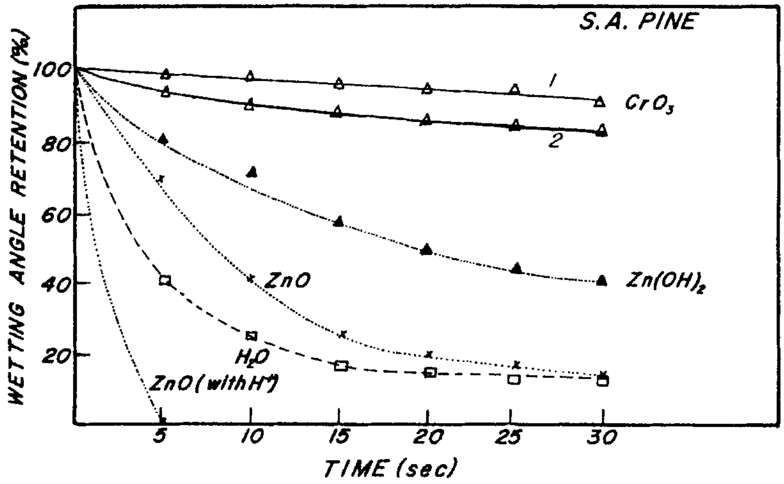


Fig 1 - Percentage wetting angle retention. S A Pine as a function of time.
1. CrO_3 10^{-1} moles/l;
2. CrO_3 10^{-2} moles/l

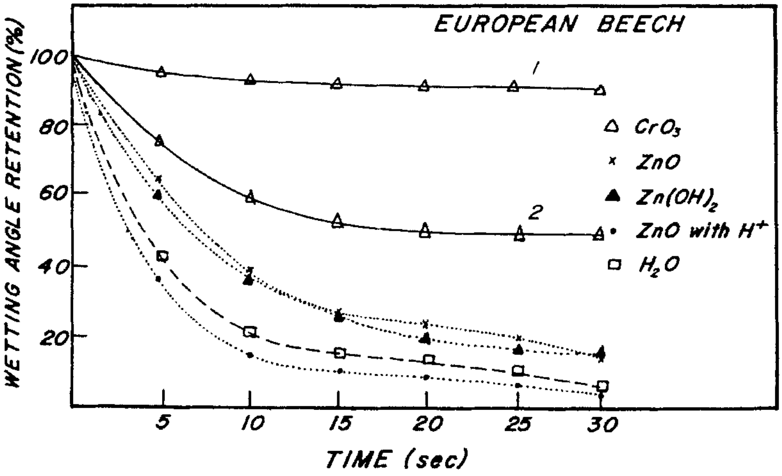


Fig 2 - Percentage wetting angle retention as a function of time. European Beech.
1. CrO_3 10^{-1}moles/l;
2. CrO_3 10^{-2} moles/l

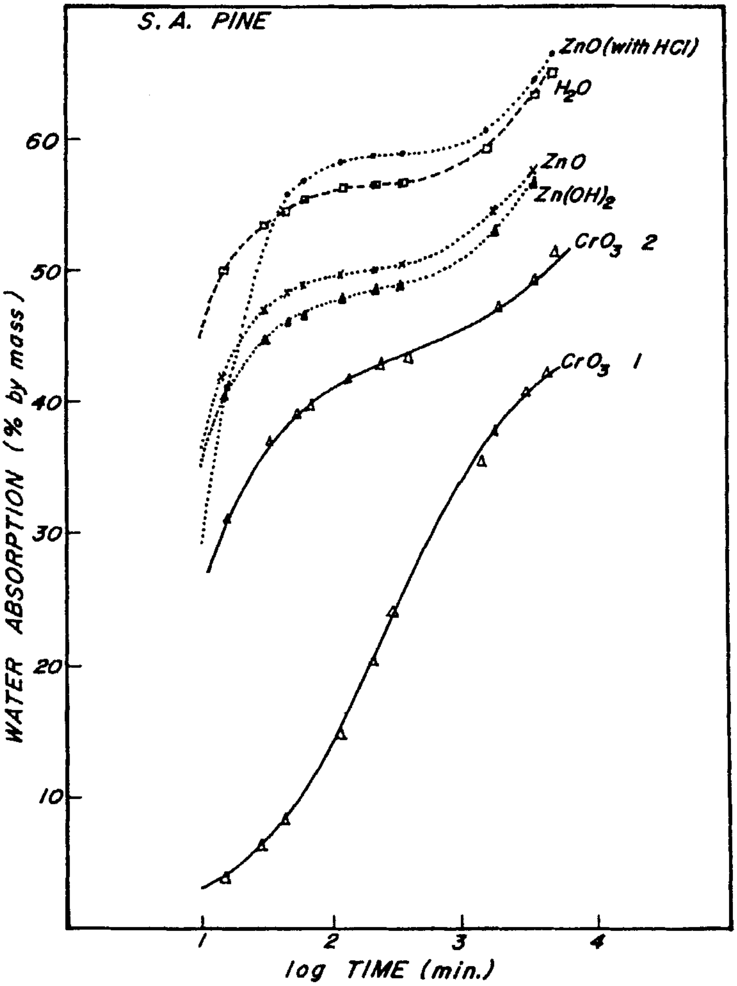


Fig 3 - Percentage water absorption as a function of time of treated and untreated S A Pine
1. CrO_3 10^{-1} moles/l
2. CrO_3 10^{-2} moles/l

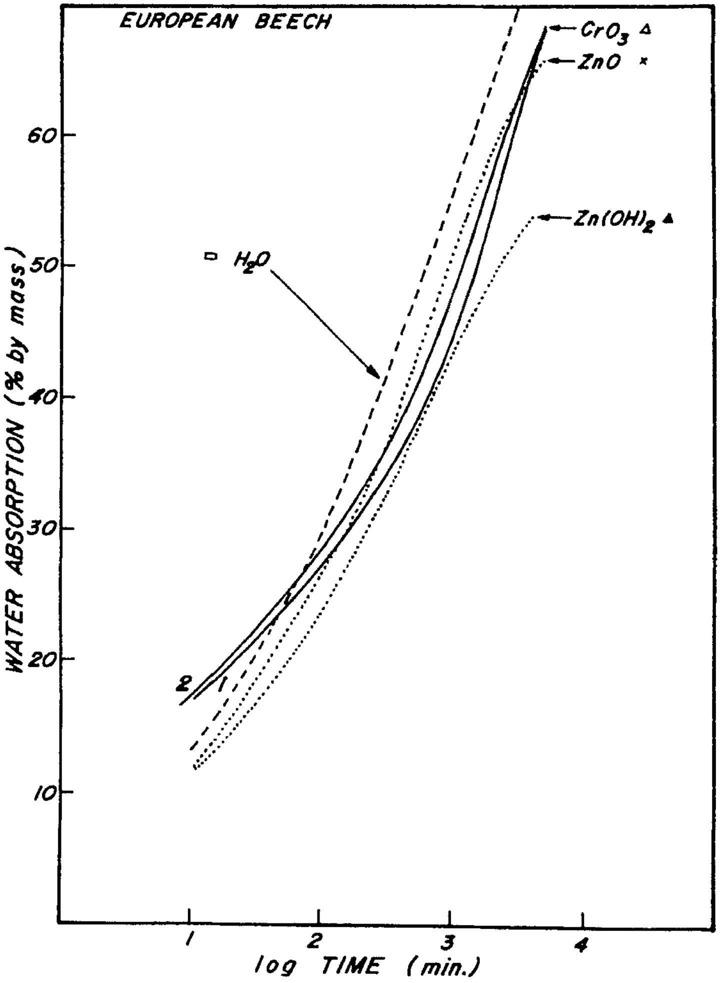


Fig 4 - Percentage water absorption as a function of time of treated and untreated European Beech.

1. CrO_3 10^{-1} moles/l
2. CrO_3 10^{-2} moles/l

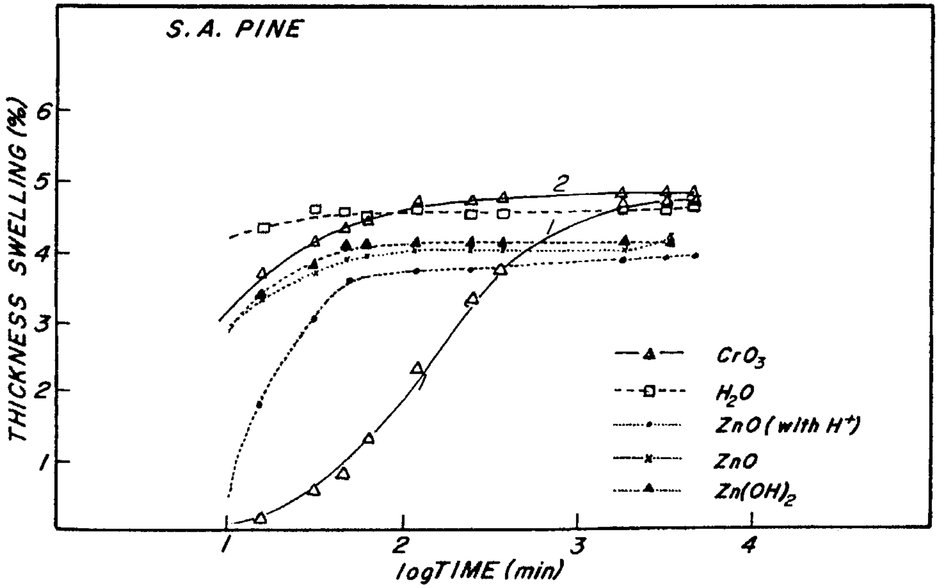


Fig 5 - Percentage thickness swelling (average of radial and tangential dimensions) in cold water as a function of time of treated and untreated S.A. Pine. 1. CrO_3 10^{-1} moles/l
2. CrO_3 10^{-2} moles/l

DISCUSSION

The reactions of a series of oxides with guaiacol were usually tried for one hour, if not otherwise indicated (see Table 1). All these oxides, with the exception of osmic tetroxide, show a low water solubility. Therefore most of the reactions had to be carried out in acid or alkaline solution, followed by neutralization. Zinc oxide as well as both the lead oxides and tin(II) oxide give insoluble compounds with guaiacol. Although zinc oxide has a low water solubility, the reaction with guaiacol was successful without acid, in a manner analogous to that in which zinc hydroxide reacts with guaiacol[6a]. Because of the low solubility of zinc oxide, the reaction time was lengthened to six days. The structure of the

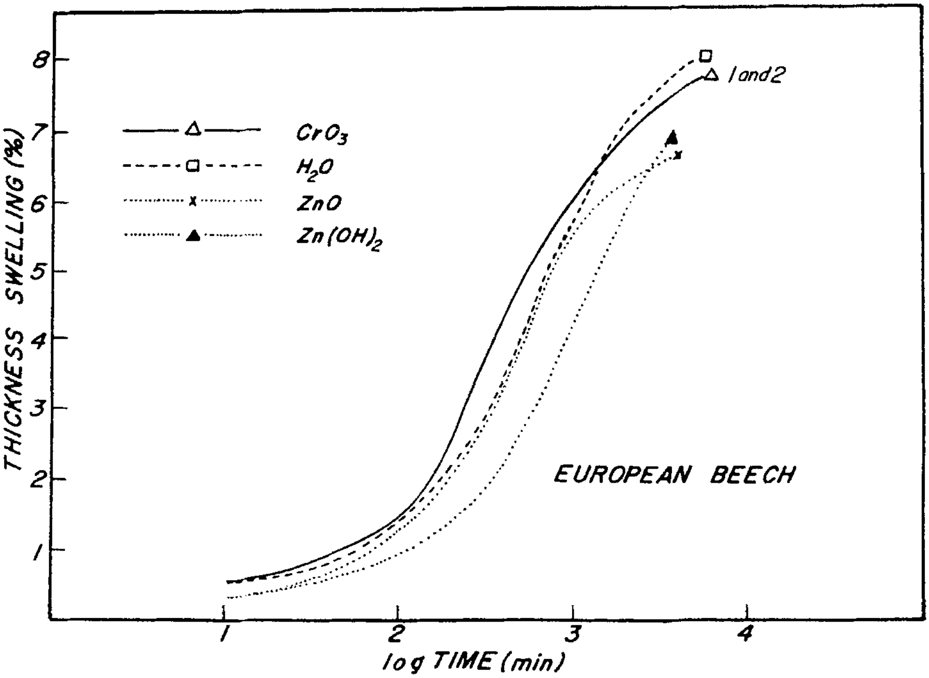
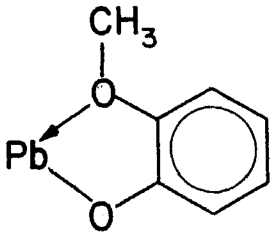


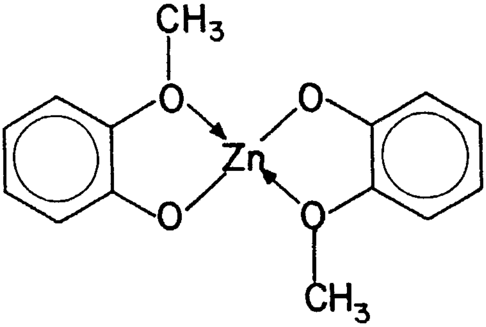
Fig 6 - Percentage thickness swelling (average of radial and tangential dimensions) in cold water as a funcion of time of treated and untreated European Beech.

complexes formed were investigated by infrared spectroscopy. Zinc and both the lead-guaiacol compounds obtained had similar IR spectra. The difference between the IR spectrum of guaiacol and the IR spectra of those metallic complexes obtained, can be seen respectively by the presence or absence of typical phenolic absorption bands. The IR spectrum of the zinc-guaiacol complex is equivalent to that of the reaction product of zinc-hydroxide and guaiacol[6b]. Two characteristic guaiacol absorption bands disappear : the deformation interaction of OH at 1330 cm^{-1} (coupled to a C = C vibration of the aromatic ring) and the shoulder absorption band of phenol at 1260 cm^{-1}

(interacting with the C - O stretching vibrations). The similarity of the IR spectra of both the lead complexes to that of the zinc complex indicates that they have a similar structure, namely:

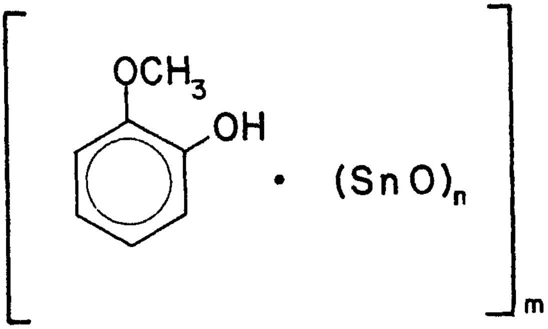


According to the elemental analysis, both the lead complexes have a metal to ligand molar ratio of 1 : 1 in contrast to the zinc complex in which the metal to ligand ratio is 1 : 2.



There are distinct differences in the IR spectrum of the tin complexes when compared with the IR spectra of the lead or zinc complex. The IR spectrum of the tin complex has generally broader bands than the other IR spectra. Most obvious is the intensive broad OH band, indicating an OH - intermolecular bond similar to that found for the CrO_3-guaiacol complex[5]. The tin complex IR spectrum is very similar to that of the

CrO_3 complex in several other points. The IR spectrum and the elemental analysis indicate the following composition:



It is not possible to give a definite formula from the available data because the reaction was incomplete, even under different experimental conditions. Furthermore, there was no way to separate the complex from unreacted tin(II) oxide and from the reaction mixture of guaiacol with four tin(II) oxide units each.

While the reaction product of chromium trioxide[5] and possibly tin(II) oxide, with guaiacol are polymeric, the products obtained from other metal oxides are not. Hence, it is expected that differences in their structures will influence their behaviour as preservatives.

Only zinc oxide and hydroxide are able to give worthwhile results when used to waterproof wood. All the other oxides gave poor results in this respect. They give either no insoluble complexes with guaiacol, hence they cannot give insoluble complexes with the guaiacol units of lignin, or there is a need of acid or alkaline solution in a large scale which not only makes the protecting process uneconomical and difficult to handle, but leaves in the wood considerable amount of H^+ and OH^- badly impairing its resistance to water. The presence of strong acids and alkali in this kind of treatment is deleterious to the wood. While the use of lead treatment gave no statistically significant improvement in water repellency of the wood, the tin oxide treatment in which, due to the reaction conditions used, considerable amounts of untreated $Sn(OH)_2$ were still present in the treated wood, actually gave water repellency worse than untreated wood. It was decided then not to carry out expensive tests with it as the continual presence of the respective hydroxide did not allow a proper evaluation of the complex formed.

The reaction of zinc oxide with guaiacol results in a "dimeric" complex. Hence, it appears that the formation of a "dimeric" complex of zinc oxide/guaiacol is the reason for the lower waterproofing ability of this compound in relation to the polymeric complex formed instead by chromium trioxide (compare Figures 3 and 5). It is possible then to advance the idea that the waterproofing ability of metallic salts and oxides is related to their ability to form insoluble complexes and to the type of structure of the complexes formed. If no complexes are formed, there is no waterproofing effect. If dimeric insoluble complexes are formed, e.g. zinc oxide, there is a retarding of the water absorption and a certain amount of waterproofing. If an insoluble polymeric complex is formed, as with chromium trioxide, more efficient waterproofing is achieved. Thus, the formation of polymeric complexes give a higher amount of cross-linking than with "dimeric" complexes. Thus, the degree of lignin cross-linking achieved is directly related to the wood waterproofing effect and its stabilization. It is possible to conclude that while extensively higher cross-linking improves waterproofing as well as dimensional stability of the wood under water attack, the insolubility of the complex formed is affected only on the waterproofing (compare Figure 3) of the wood but not on its dimensional stability (compare Figure 5). The effect given by cross-linking is definitely more marked on water repellency (compare Figures 1 and 2) than is the formation of insoluble compounds, i.e. both zinc and chromium form insoluble compounds but chromium trioxide is a better waterproofer.

It is interesting to compare the speed of reaction of at least one of such oxides, CrO_3, with cellulose and lignin, for which kinetic data about both reactions do exist. The reaction or CrO_3 with d(+)-glucose as a model compound of cellulose at 70°C takes place in a time range of 1-4 hours[7,8], while at the same temperature the reaction of guaiacol as a model compound of lignin with CrO_3, and at a concentration of both reagents of only $^1/_{10}$ of that used for glucose, takes place in a time range of 5-15 minutes[7]. At identical concentrations and under identical reaction conditions the reaction of CrO_3 with guaiacol and the guaiacol units of lignin has been found to be 1.2×10^3 times faster than the reaction of CrO_3 with d(+)-glucose and cellulose[7,9].

Thus, since the amount of cellulose in wood is approximately three times that of lignin of which only 30% - 40% of the lignin content is composed of guaiacol units[10], the proportion of CrO_3 reacting with lignin in wood, assuming a constant supply of oxide molecules, is approximately 120 times greater than the amount reacting with cellulose.
If phenomena such as absorption and localized reactions on the cellulose are considered, the disproportion in the amount of oxide reacting with the two major wood components is probably lower than 120 to 1, but nevertheless still quite considerable.

It is then quite clear that while a small degree of water repellency is certainly imparted to the wood also by the reaction of the oxide with cellulose, this effect is indeed minor when compared to the major effect due to the considerably faster reaction of the oxide with lignin groups.

It is also interesting to note that other authors[11], although dealing with quite a different type of system, namely a Zn-NH_3 complex in which NH_3 and ammonium compounds were used to both form a Zn-NH_3 complex as well as to facilitate solution of the ZnO used to form such a complex, have found that bonds between a Zn-based system and wood are stronger than between water and wood. However, due to the particular experimental method used, they could not define the nature of the interaction between Zn and wood nor which of the wood components was more likely to be involved in the waterproofing mechanism. Their and our findings appear to indicate that many, if not all wood waterproofing systems in which Zn is involved, are able to form a percentage of stable complexes with wood provided that a strong acid residue is not still present in the wood after the end of the treatment.

From the different figures it is also possible to note that an increase in the concentration of CrO_3 from 10^{-2} to 10^{-1} improves the waterproofing and water repellency of the wood. This fact is in agreement with that discussed as a higher amount of lignin cross-linking and of insoluble complex are formed by increasing the concentration of the treating solution.

The difference in the results obtained with beech and pine might appear strange. Namely, while both CrO_3 treated beech and pine show good water repellency and comparable wetting angle retention (compare Figures 1 and 2) their water absorption behaviours are quite different (compare Figures 3 and 4). The water absorption of the pine specimens is reduced by the oxide treatment. This is not the case with beech. While faster end grain penetration should be expected in the case of the more porous and less dense pine wood used, the peculiar anatomy of beech wood must also be kept in mind. In the structure of beech a great amount of comparatively big rays are present which considerably facilitate fast water penetration in the specimens. Thus, while the cell walls of beech will be waterproofed just as efficiently as those of pine as showed by the wetting angle results, the water absorption results are affected by the faster water penetration through the beech rays. This is quite likely the main contributing cause to the difference in water absorption results.

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