

EVOLUTION OF CHLORINATED PHENOLS FROM CONCENTRATED BORON SOLUTIONS CONTAINING THESE PHENOLS ADDED AS THEIR SODIUM SALTS

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ABSTRACT

Sodium salts of chlorinated phenols are added to the solutions for boron diffusion treatment of timber for added protection against moulds and sapstain fungi. The evolution of chlorinated phenols from the treating solutions was studied under laboratory conditions and it was found that their concentration in air above the solutions can be reduced to a safe level by increasing the pH of a solution.

INTRODUCTION

One of the commercial treatments used against insects and decay fungi in wood preservation is the diffusion of boron compounds (British Wood Preservers Association). To be able to maintain the required high boron concentration in the treating solution, a formulation of boron compounds with high solubility is necessary. Formulations based on sodium salts of boric acid should have a $\text{Na}_2\text{O} : \text{B}_2\text{O}_3$ ratio of between 1 : 4 and 1 : 5. The most common formulation is "Timbor", a proprietary preparation of sodium octaboratetetrahydrate ($\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$).

For treatment, the solution is applied at a concentration of 20 to 40% (expressed as boric-acid equivalent), depending on the size of the timber. To dissolve and keep boron in solution at the highest concentration, the solution has to be heated to a minimum of 57°C.

The period required for the diffusion of boron into wood varies from 4 to 12 weeks, depending on the thickness of timber (British Wood Preservers' Association; New Zealand Timber Preservation Authority, 1955). During this period, the timber has to remain wet. Since boron is not toxic to all wood-inhabiting fungi during this storage period, boron-tolerant fungi can colonise and grow in the treated wood (British Wood Preservers' Association; New Zealand Timber Preservation Authority, 1955; MacLean, 1962). To prevent fungal growth during this period, it is recommended that a sapstain and mould preventative be added to the treating solution. At present most sapstain and mould preventives contain a chlorinated phenol as the active ingredient. When used alone on unseasoned lumber, the solutions of the sodium salts of chlorinated

phenol are unheated and are buffered to about a pH of 10. At this high alkalinity, the chlorinated phenols exist as their sodium salts and no evolution of these phenols from the treating solution can occur. However, the pH of fresh Timbor solutions is approximately 7 and under this near-neutral condition, a portion of the chlorinated phenols may exist in free phenolic form, and so may escape with water vapour from the heated solutions. Odour, noticed at dip tanks during the treatment of lumber in sawmills, suggested that chlorinated phenols were present in the air.

To obtain information about the concentration of chlorinated phenols in the atmosphere above dip tanks, laboratory experiments were carried out using the sodium salts of tetra- (TCP) and pentachlorophenol (PCP). These two phenols are the main toxic ingredients in sapstain- and mould-preventive formulations in use today.

EXPERIMENTAL

Two experiments were undertaken, one using technical-grade PCP and the other using technical-grade TCP, both in solutions of Timbor prepared according to British Wood Preservers' Association standard. The temperatures and concentrations of the solutions (200 ml) were maintained as shown in Table 1 in an Erlenmeyer flask (1-litre) using a water bath (Fig. 1). The surface area of the solution was approximately 100 cm². To ensure that the evaporated chlorinated phenol was not condensed in significant amount in the Erlenmeyer flask and washed back to the solution, compressed air was blown into the flask about 1 cm above the surface of the solution, at a rate of 300 ml/min, for a period of 7½ hours. The arbitrary air-flow rate was selected to change the air in the flask about every three minutes. During the period about 0.13 m³ of air was used.

The condensed vapour was collected in a flask to which was attached a gas-washing bottle containing 0.02% NaOH solution to trap any remaining PCP or TCP in the air (Fig. 1). In these experiments, the pH of the solution was measured and found to

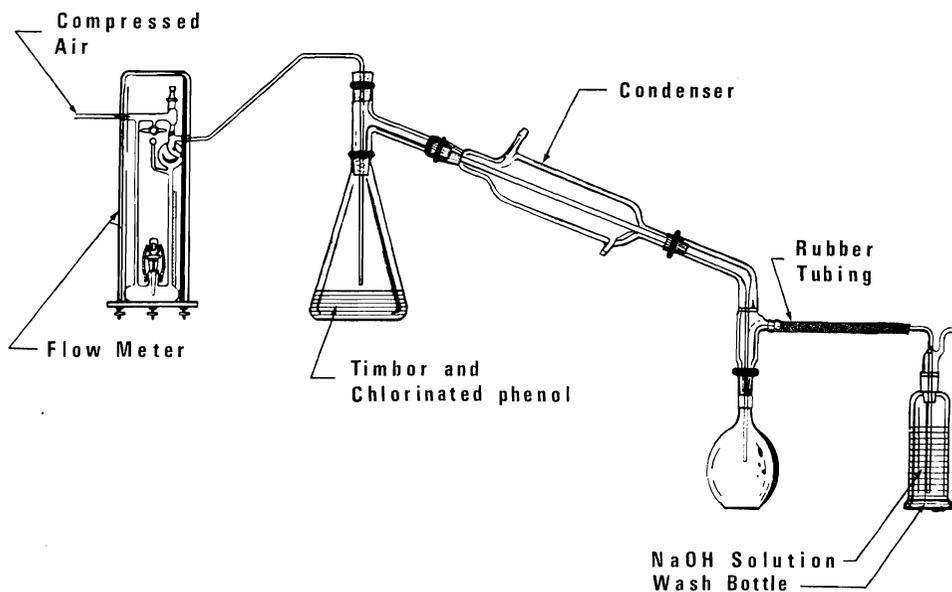


FIG. 1—Experimental equipment.

vary between 7.0 and 7.2. To obtain information on the effect of pH on the volatilisation of chlorinated phenols, in another experiment the pH of the solutions was adjusted to 7.5 and 8.0 with sodium hydroxide solution. This experiment was made using only the two temperatures 50°C and 70°C with the corresponding concentration of Timbor in the first experiment (Table 1).

At the end of the experiment, the condenser was washed with acetone. The condensates, NaOH solution from the gas-washing bottle and the acetone washing were combined. After evaporation of the acetone under reduced pressure, the alkaline solution was acidified and extracted with ether. The volume of the ether was adjusted to 25 ml.

From this extract, a 5 to 200 μ l sample was transferred to a small test tube and the ether was evaporated at room temperature using a gentle air stream. The residue was silylated with 0.1 ml bis-(trimethylsilyl)-acetamide in the stoppered test tube. To ensure complete reaction, the test tube was heated to 60°C in a water bath for 20 min. The volume of the silylated solution was made up to 1 ml with ethyl acetate. The concentration of TCP and PCP was determined by gas chromatography using an electron-capture detector (Cserjesi and Johnson, 1972).

TABLE 1—Concentration of Timbor and chlorinated phenols and the temperature of the solutions used for the tests

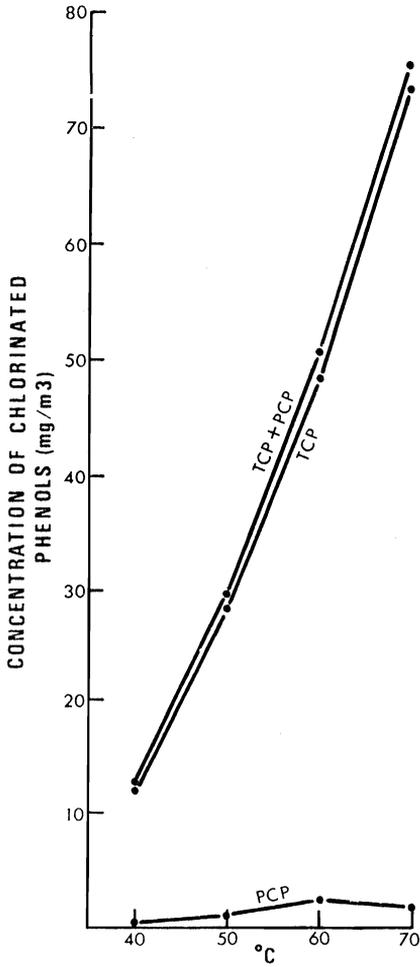
Concentration of Timbor (boric acid equivalent) %	Concentration of chlorinated phenols %	Temperature °C
20	0.5	40
27.5	0.5	50
40	0.5	60
40	0.5	70

RESULTS AND DISCUSSION

The experiment showed conclusively that chlorinated phenols are lost from the treating solution and that this loss increased with increasing temperatures (Fig. 2 and Table 2). It is interesting to note that the TCP concentration in the air above a solution of Timbor to which technical-grade PCP was added is higher than that of PCP. TCP as an impurity in the technical-grade PCP preparations used was 16%, but it can be as high as 20%. The greater volatility of TCP from the Timbor solution explains its higher concentration in the vapours. In our experiments, TCP was not exhausted from the solution, since out of approximately 200 mg added with PCP, less than 20 mg had evaporated in 7½ hours at 60°C, close to the highest temperature recommended for Timbor treating solutions. The air over the solutions to which technical-grade TCP was added contained only a very small amount of PCP.

The maximum allowable concentration of PCP in the atmosphere, according to British Columbia Workmen's Compensation Board regulations (1972) and the recommended threshold limit values in workroom air in the USA (American Conference of

timbor and tech. grade
tetrachlorophenol



timbor and tech. grade
pentachlorophenol

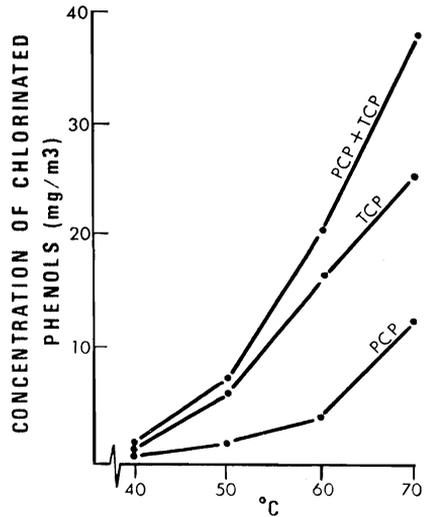


FIG. 2—Tetra- and pentachlorophenol concentration in air above solutions containing Timbor and technical tetra- or pentachlorophenol heated to different temperatures (see Table 1). pH of the solutions was not adjusted.

TABLE 2—Concentration of tetrachlorophenol (TCP) and pentachlorophenol (PCP) in air above solutions containing Timbor and technical TCP and PCP heated to 50°C and 70°C, determined in experiments as described in text. The pH of the solutions was adjusted to 7.5 or 8.0

Solution	Chlorinated phenol concentration (mg/m ³)						
		at 50°C			at 70°C		
	PCP	TCP	Total	PCP	TCP	Total	
Timbor + TCP	pH 7.5	none	4.3	4.3	none	20.0	20.0
	pH 8.0	none	3.4	3.4	none	3.7	3.7
Timbor + PCP	pH 7.5	none	0.2	0.2	1.8	2.8	4.6
	pH 8.0	trace	0.1	0.1	0.1	0.2	0.3

Industrial Hygienists, 1971; Gleason *et al.*, 1969) is 0.5 mg/m³. Although no value was found for the toxicity of TCP, it was assumed that its toxicity is equal to that of PCP. At 60°C we detected 40 (for PCP) and 100 (for TCP) times greater concentrations in our experiments than the maximum allowable for chlorinated phenols above solutions with no pH adjustment. The adjustment of the pH of Timbor solution may lower the chlorinated phenol concentration below the recommended threshold limit (Table 2). The pH of the solution, however, may change and for safety, even when the pH is adjusted to higher values, the necessity of good ventilation has to be emphasised. This ventilation should not depend on natural air movement, since in calm weather workers close to a treating tank may be exposed to greater chlorinated-phenol concentrations than the regulation allows.

TCP, because of its greater volatility than PCP, exposes workmen to much more danger and therefore should not be used in Timbor treating solutions. The higher volatility of TCP resulted in this phenol being the main component in the air above the treating solution to which technical PCP was added. Using a preparation of PCP which has low TCP impurities, and to adjust pH of the treating solution to 8, would lower the concentration of chlorinated phenols in the air of the working area. However, good ventilation still remains imperative.

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