

SD 433

452

1222

# **SOME TOXICITY DATA AND THEIR PRACTICAL SIGNIFICANCE**

**Information Reviewed and Reaffirmed**

**April 1953**

**INFORMATION REVIEWED AND  
REAFFIRMED JUNE 1959  
DATE OF ORIGINAL REPORT  
JANUARY 19, 1937**



**No. R1222**

**UNITED STATES DEPARTMENT OF AGRICULTURE  
FOREST SERVICE  
FOREST PRODUCTS LABORATORY  
Madison 5, Wisconsin  
In Cooperation with the University of Wisconsin**

# SOME TOXICITY DATA AND THEIR PRACTICAL SIGNIFICANCE<sup>1</sup>

By

ERNEST BATEMAN, Senior Chemist

and

R. H. BAECHLER, Chemist

Much of the toxicity work of the Forest Service at the Forest Products Laboratory has been aimed toward a better understanding of the natural laws of toxic action. To this end the compounds tested were chosen for their chemical constitution rather than for their probable value as wood preservatives and, as might be expected, many compounds which have been found to be toxic cannot be recommended for practical use because of some undesirable property. Thus many compounds are excluded by their injurious effects upon wood. All of the mineral acids as well as salts with strongly acidic reactions, such as the soluble salts of aluminum, iron, and tin, are very toxic to fungi, but they attack wood and slowly lower its mechanical strength. The same holds for alkalies and strongly alkaline salts such as sodium carbonate and trisodium phosphate. There are certain acid-reacting salts whose use is limited by the corrosive action of their solutions on steel. Examples of this latter type are salts of mercury,<sup>2</sup> copper, nickel, cobalt, and antimony. Some toxic compounds -- among them potassium permanganate, catechol, pyrogallol, o-aminophenol, o-phenylenediamine, 2-4 dichloraniline, and 2-4-6 trichloraniline, sodium bisulphite -- are considered lacking in adequate chemical stability. The list of chemicals that are sufficiently toxic, but too volatile to be used as wood preservatives is very large. It includes benzene, toluene, xylene, phenol, o-, m-, and p-cresol, chlorbenzene, nitrobenzene, benzaldehyde, o- and p-chlorophenol, o- and p-nitrophenol, o- and p-nitrochlorbenzene, p-nitrobenzaldehyde, p-nitraniline, o- and p-chloraniline, iodine, the lower aliphatic hydrocarbons, and many others. Another large list comprises those toxic compounds that would merit serious consideration were it not for their high cost. This list includes thymol, pyridine mercuric chloride, benzyl aniline, mercurochrome, alpha naphthol, benzoic acid and certain substituted benzoic acids, picric acid and soluble picrates, soluble molybdates, and the soluble salts of cadmium, cobalt, uranium, thallium, thorium, silver, and gold. The membership of this group is not fixed, but will change with changes in market conditions.

---

<sup>1</sup>Presented at the 33rd annual meeting of the American Wood-Preservers' Assn., New Orleans, La., Jan. 26-28, 1937, and published in A.W.P.A. Proceedings 1937.

<sup>2</sup>These salts may be used in special treating-plant equipment or, in some cases, in steel equipment after a bichromate or ammonia has been added.

The compilation of toxicity and cost data included in this report covers all those compounds that would seem to offer any promise as wood preservatives after their toxicity, present cost, volatility, solubility in a cheap vehicle, corrosiveness to metals, effect on wood, and health hazard have been considered.

Several of the compounds in the list are of proven value and serve as standards of comparison, several are being tested in service, and several have been tried and found wanting. The latter are included to illustrate the fallibility of predictions concerning the performance of a wood preservative when based solely on laboratory data.

A toxic chemical of low volatility may fail to prevent the decay of wood for any of several reasons; e.g.:

1. While it is sufficiently soluble in distilled water, it may be insufficiently soluble in natural waters because of their salt content or alkalinity.
2. It may be insufficiently soluble in some temperature range below 28 deg., which permits growth of wood-destroying fungi.
3. It may be insufficiently toxic against some fungi other than the test organisms, even though the latter is one of the more resistant fungi and toxicity tests are made under conditions as favorable as possible to the organism.
4. It may be changed to some nontoxic compound by chemical reaction with some constituent of wood. Then, too, even though a chemical prevents decay, it may, over a long period of time, have some unforeseen deteriorating action on wood. It is thus apparent that service tests are necessary to establish the effectiveness of a material as a wood preservative.

In the accompanying table the killing point designates the concentration in nutrient agar necessary to kill a transplant of the fungus, Madison No. 517.<sup>3</sup> The TIP (total inhibition point) designates the concentration necessary to inhibit the growth of the same organism on nutrient agar. It has been chosen in preference to the killing point as the index of a chemical's toxic effect for the reason that its value has been determined for each chemical under discussion when the solubility permitted, whereas the killing points of many are unknown. Cost figures are taken chiefly from the Oil, Paint & Drug Reporter of Nov. 16, 1936. Costs are based on large quantities and corrections have been made for the water of crystallization in the salts. The figure for the cost times TIP will be designated in the remainder of this discussion as the "cost per unit of toxicity."

---

<sup>3</sup>This is the organism used in all previous work by either of the authors.

Table 1.—Cost, toxicity, and unit cost of preservative materials

Name	Formula	Killing point	T.I.P.	Cost	Unit Cost	Remarks
		Percent anhydrous	Percent anhydrous	Cents per pound anhydrous	Cost x T.I.P.	
WATER SOLUBLE						
Arsenic trioxide .....	As <sub>2</sub> O <sub>3</sub>		0.025	3.5	0.088	Readily soluble only in alkaline solution. Health hazard.
Borax (sodium tetraborate)...	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	0.13	.083	1.5	.12	Seems to shorten life of paint. May be injurious to wood.
Boric acid .....	H <sub>3</sub> BO <sub>3</sub>	.25	.13	5.2	.68	
Cadmium chloride .....	CdCl <sub>2</sub> ·2H <sub>2</sub> O		.078	60.0	4.7	May protect against insects as well as decay.
Copper sulphate .....	CuSO <sub>4</sub> ·5H <sub>2</sub> O		.064	6.5	.42	Corrosive to steel.
Mercuric chloride .....	HgCl <sub>2</sub>		.005	99.0	.50	Corrosive to steel.
Nickel chloride .....	NiCl <sub>2</sub>		.0136	33.0	.45	Corrosive to steel.
Sodium arsenite .....	Na <sub>2</sub> AsO <sub>3</sub>		.044	3.5	.15	Health hazard.
Sodium chromate .....	Na <sub>2</sub> CrO <sub>4</sub>	.034	.021	6.0	.12	Alkaline reaction. Does not seemingly react with wood.
Sodium dichromate .....	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	.03	.018	6.1	.11	Acid reaction. Is reduced by wood.
Sodium fluoride .....	NaF	.25	.24	7.2	1.7	
Sodium tetrachlorophenolate ..	C <sub>6</sub> HCl <sub>4</sub> ONa	.002	.002	18.0	.036	
Sodium pentachlorophenolate ..	C <sub>6</sub> H <sub>5</sub> ONa	.002	.002	18.0	.036	
Thallium sulphate .....	Tl <sub>2</sub> SO <sub>4</sub>		.023	1		
Zinc chloride .....	ZnCl <sub>2</sub>	.35	.35	4.5	1.6	
Zinc acetate .....	Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>		.47	7.4	3.5	Improves seasoning characteristics of wood.
WATER INSOLUBLE - ACID SOLUBLE (May be formed in wood by double treatment)						
Magnesium ammonium arsenate ..	MgNH <sub>4</sub> AsO <sub>4</sub>		.067	1		Acid solution not very corrosive to steel.
Basic nickel chromate .....			.012	1		Also soluble in ammonium hydroxide.
Ammoniated nickel arsenate .....			.03	1		Also soluble in ammonium hydroxide.
Nickel ammonium phosphate .....	NiNH <sub>4</sub> PO <sub>4</sub>		.2	1		Also soluble in ammonium hydroxide.
OIL SOLUBLE						
Acenaphthene .....	C <sub>10</sub> H <sub>8</sub> (CH <sub>2</sub> ) <sub>2</sub>		1	1		
Betanaphthol .....	C <sub>10</sub> H <sub>7</sub> OH	.015	.013	24.0	.31	B.P. 280°. Mild odor. Slowly turns dark.
1-Chlorbetanaphthol .....	C <sub>10</sub> H <sub>6</sub> ClOH	.005	.005	1		
Coal tar creosote .....		.07	.05	1.3	.065	
Alphachloronaphthalene .....	C <sub>10</sub> H <sub>7</sub> Cl	.006	.006	1		B.P. 263°. Mild odor.
2-4 Dichloroalphanaphthol ...	C <sub>10</sub> H <sub>5</sub> Cl <sub>2</sub> OH		.002	1		Practically odorless. Solubility in water extremely low.
2-6 Dichloro-4-nitrophenol ..	C <sub>6</sub> H <sub>2</sub> Cl <sub>2</sub> NO <sub>2</sub> OH		.01			
2-6 Dinitrophenol .....	C <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> ) <sub>2</sub> OH	.023	.023	23.0	.53	
2-4 Dinitrochlorbenzene .....	C <sub>6</sub> H <sub>3</sub> Cl(NO <sub>2</sub> ) <sub>2</sub>	.01	.01	14.0	.14	
Diphenyl .....	C <sub>6</sub> H <sub>5</sub> ·C <sub>6</sub> H <sub>5</sub>		1	15.0		
Naphthalene .....	C <sub>10</sub> H <sub>8</sub>		.003	3.0	.01	
Nitrobetanaphthol .....	C <sub>10</sub> H <sub>6</sub> NO <sub>2</sub> OH		.016	1		
Nitroluene (mixed) .....	C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> NO <sub>2</sub>		.04	10.5	.8	B.P. 220°-237°.
Orthophenyphenol .....	C <sub>6</sub> H <sub>4</sub> OHOC <sub>6</sub> H <sub>5</sub>	.015	.013	22.0	.29	
Tetrachlorophenol .....	C <sub>6</sub> HCl <sub>4</sub> OH	.002	.002	14.0	.04	
Pentachlorophenol .....	C <sub>6</sub> H <sub>5</sub> OH	.002	.002	14.0	.028	
Trichlorbenzene (1-2-4) ....	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	.007	.007	1		B.P. 213°.

<sup>1</sup>Price quotations on chemical in technical grade not available.

<sup>2</sup>Exact T.I.P. (total inhibition point) unknown but excess of chemical inhibits growth of fungus.

<sup>3</sup>Saturated solution permits feeble growth.

<sup>4</sup>Saturated solution -- permits no growth at 32° but spore growth at 25°.

## Discussion

In considering the table, it is necessary to keep in mind the different methods of treatment and the varied requirements of the preservative, depending upon the conditions under which the treated wood is to be used. Proposed preservatives accordingly fall into several classes.

A toxic chemical that is soluble in petroleum oils may be dissolved in fuel oil or spent crank-case oil to produce a preservative that may be used in place of creosote. The chief advantage a preservative of this kind might have over creosote would be that of cost; accordingly a chemical to be so used must be cheap.

A toxic chemical that is soluble in a volatile solvent that does not swell wood may be used to treat kiln-dried stock or fabricated material, such as window sash and automobile bodies. For these uses its price is of less importance, but it should be practically odorless and paintable.

A water-soluble salt may be used in a standard pressure treatment of wood to be used where leaching is not too rapid. If its solubility is favorable, it may be used to treat green material by a steeping process.

A water-soluble salt that can be converted to an effective compound of low solubility by an after treatment may find use under conditions favorable to leaching.

A chemical may be found to be insecticidal as well as fungicidal in which event it may be used to protect wood against termites or other insects.

A toxic chemical may possess some other desirable property, such as fire retardance or reduction of seasoning defects.

The significant properties of the more promising materials will now be reviewed.

## Oil-Soluble Compounds

### Tetrachlorophenol

Of all the compounds that were found to kill our test organism, tetrachlorophenol and pentachlorophenol are the cheapest sources of toxic action. A solution of tetrachlorophenol in gas oil of such strength as to equal creosote in toxicity would be a little cheaper on the basis of current prices than creosote bought in large quantities. Since the highly satisfactory performance of creosote has been established by extensive use, a change to this unproven substitute would not be indicated for users of large quantities of preservative. It might be attractive to a treating plant located a considerable distance from a source of creosote, but

relatively near an oil refinery even under present market conditions with the price of creosote relatively low. During times when the price of creosote is much higher than at present, an oil solution of tetrachlorophenol could well be an economical substitute in most localities. Information on its effectiveness would then be needed, for which reason extensive service tests on several concentrations of the chemical in oil should be started as soon as possible. Several hundred fence posts treated with it have been put into test, some in Wisconsin and the rest in the Southern Forest Experiment Station. It seems especially promising for this use because of the differential in the cost to the farmer of creosote bought in small quantities and spent crank-case oil. It could also be used dissolved in a volatile solvent to give wood a treatment which would be clean, paintable, and resistant to leaching. Its use in this form would be restricted by its unpleasant odor to some types of industrial buildings, sign posts, and the like.

#### Pentachlorophenol

Pentachlorophenol is a comparatively new industrial product and has not as yet been studied very thoroughly in this Laboratory. It resembles tetrachlorophenol chemically and physically and also in its toxicity. The toxicity of its petroleum-oil solution, which would be governed in part by the distribution coefficient, has not been determined. Its odor is less pronounced than the odor of tetrachlorophenol. From the data available the two chemicals are about equally promising. One hundred fence posts have been treated with a 3 percent solution and another hundred with a 5 percent solution of pentachlorophenol and installed in a service test in the Southern Forest Experiment Station. Similar tests should be started in other parts of the country and should be supplemented by tests on wood treated with a solution of the chemical in a volatile solvent.

#### 2-4 Dinitrochlorbenzene

2-4 dinitrochlorbenzene is fairly cheap per unit of toxicity. It shows some tendency to react with water, the chlorine being replaced by hydroxyl to form dinitrophenol; this reaction is very slow at ordinary temperatures and in the absence of alkali. Its odor is mild and not unpleasant. It seems more likely to prove useful as a toxic to be used in a clean treatment than as a toxic to be added to a crude oil carrier. For the latter use it offers no apparent advantages over tetra- or pentachlorophenol and is more expensive. However, an extensive series of service tests could well include both types of treatments.

#### Beta Naphthol

Beta naphthol is already being used in the treatment of automobile bodies and window sash. It seems to be giving good results. It is not readily soluble in volatile petroleum distillates, but its solubility is greatly increased by the addition of about 10 percent of pine oil to the

solvent. Its tendency to turn to a reddish color is a disadvantage in some cases. There is no urgent need for service tests on it, but tests comparing it with other preservatives would be of some value.

#### Orthophenylphenol

Orthophenylphenol is similar chemically to beta naphthol in that it consists of two benzene rings joined together and contains one hydroxyl group replacing a hydrogen. The two are similar in toxicity and happen to sell for about the same price.

#### Dinitrophenol

Dinitrophenol is an ingredient of certain proprietary preservatives. Its cost is moderate. Service tests on it alone would be of interest.

#### Naphthalene

Naphthalene, while inherently very toxic, is not soluble enough to kill the test organism in laboratory tests; indeed, it permits a sporulated growth. These tests are carried out with conditions of temperature, moisture, and food supply as favorable as possible to the organism; under service conditions this organism or any other wood-destroying fungus might fail to grow on wood in the presence of an excess of naphthalene. Service tests on wood treated with a solution of naphthalene in a volatile solvent would answer this question. In addition to establishing the value or lack of value of naphthalene alone they would be of theoretical interest in throwing light on the part naphthalene plays in the action of creosote. Since a saturated solution of naphthalene in water is hardly sufficient for total inhibition under laboratory conditions, a solution of it in a fixed oil would have to be saturated to be a likely preservative. With naphthalene as cheap as creosote, such a solution would not be impractical from a cost standpoint. Probably the most promising field for naphthalene lies in mixtures with other toxic materials. A mixture of 1 gal. of fuel oil, 1 lb. of naphthalene, and 1/3 lb. of tetrachlorophenol is almost as toxic as creosote and is somewhat cheaper at present. It resembles creosote in that it contains a toxic hydrocarbon and a toxic high-boiling phenol, both dissolved in an inert oil of low volatility.

#### Mixtures of Cyclic Hydrocarbons

It has been shown that in mixtures of hydrocarbons each individual exerts its toxic effect independently of the others. According to Bateman and Henningsen "the percentage of growth of a fungus subjected to a mixture of hydrocarbons appears to be the product of the percentage growths of the fungus when subjected to each component separately." This product must be more than zero; in other words, there must be some growth so long as the mixture contains no individual which completely inhibits growth.

Here again we may hazard the assumption that under service conditions growth of the fungus may be completely inhibited by chemicals which would permit a slight growth in the laboratory. The following mixtures of hydrocarbons have been found to permit only a very feeble growth of the test organism on nutrient agar and may be recommended for service tests: (1) naphthalene + diphenyl, (2) naphthalene + acenaphthene, (3) acenaphthene + diphenyl.

The following chemicals are not quoted in price lists of industrial chemicals, since they have no technical use; consequently, their costs per unit of toxicity cannot be calculated. In each case the method of preparation is simple enough to lead one to believe that any material might be produced cheaply enough on a large scale. Any of them might prove to be suitable for specific uses and they are recommended for field tests in that spirit.

#### Chlornaphthalene

Both alpha and beta chlornaphthalene are very toxic, the alpha being the more toxic of the two. They boil at 263 deg. and 265 deg., and so their permanence is questionable. The material to be used in tests would preferably be the crude mixture made under conditions yielding the highest possible proportion of the alpha compound.

#### 1-Chlorobetanaphthol

1-chlorobetanaphthol, made by chlorinating betanaphthol, is more than twice as toxic as betanaphthol. It has a low vapor pressure which promises permanence and accounts for its mild odor despite the presence of hydroxyl and chlorine in the same ring. Its most important advantage over betanaphthol lies in the fact that it may be dissolved in petroleum distillates without the addition of pine oil.

#### Nitrobetanaphthol

Nitrobetanaphthol has about the same toxicity as betanaphthol. It may be more permanent, since it is lower in solubility and volatility. It is only moderately promising.

#### 2-6 Dichlor-4-nitrophenol

2-6 dichlor-4-nitrophenol is not as toxic as tetrachlorphenol and seems less promising. A possible virtue is the presence of two toxicity increasing groups (chlor and nitro) in the molecule which may increase the number of fungi toward which it is very toxic. Also it has a fairly mild odor.



### Trichlorbenzene

Of the three isomers having this formula the 1-2-4 and the 1-3-5 compounds have been tested and were found to be very toxic. They boil slightly below naphthalene and would, therefore, be expected to be only fairly permanent.

### Nitrotoluene

Both ortho and paranitrotoluene are about as toxic as creosote. Their odors are very agreeable, but might be objectionably strong in poorly ventilated interiors.

### 2-4 Dichloralphanaphthol

2-4 dichloralphanaphthol is one of the most toxic materials thus far tested. It is practically odorless and colorless. It would seem suitable wherever there is need for an odorless, paintable preservative soluble in a liquid that does not swell wood. Its cost in large quantities would probably be moderate, since the process of making it is fairly simple and does not require any expensive materials. Its solubility in water is extremely low; in fact, barely sufficient to yield an agar solution toxic to the test organism. It might prove to be insufficient to inhibit the growth of some other fungus in wood. This low solubility in water is a virtue from the standpoint of permanence and probability of chemical effect on wood, glue, and finishes, but, on the other hand, as it is coupled with a high solubility in petroleum oils it results in a distribution coefficient so high that the percentage necessary to produce a toxic mixture with a permanent petroleum oil is prohibitively high. For this reason it should be dissolved only in a volatile solvent.

### Water-Soluble Compounds

Water-soluble compounds can be used in aqueous solution. Some are quite soluble in certain organic liquids and thus might answer the need for an odorless treatment for kiln-dried wood.

### Arsenic Trioxide and Arsenites

Arsenic trioxide combined with sodium arsenite (arsenic trioxide alone dissolves in water with great difficulty) offers toxicity to the test organism at the lowest cost of all the inorganic compounds studied. It is generally toxic to insects, but has not given a very good account of itself in termite tests conducted by Hunt and Snyder. This may be due to leaching. Its effectiveness as a preservative is being tested in numerous installations including a group of 200 ties in a test trace at Madison, Wis.

### Boric Acid and Borax

Borax has a low cost per unit of toxicity -- about one-third that of zinc chloride. It is not very toxic to higher animals. It is chemically stable and its solutions are noncorrosive to steel. Two hundred red oak ties treated with borax were placed in a test track at Madison, Wis., 7 years ago. So far they have lasted as well as similar ties treated with zinc chloride. Sapling tests reported by the Bell Telephone Laboratories give borax a rating inferior to zinc chloride. Borax has one property that is a drawback, namely, its alkalinity which affects paint-holding properties and might result in a gradual weakening of wood treated with the salt. The difficulty might be avoided by the addition of sufficient boric acid to form a neutral mixture. A 1:1 mixture of borax and boric acid is soluble to the extent of 12.5 percent at 25 deg. C. Its toxicity is almost equal to that of borax. Service tests and painting tests on wood treated with a neutral mixture are indicated, irrespective of the findings on the durability of ties treated with straight borax.

### Cadmium Chloride

Cadmium salts lie between the salts of zinc and mercury in their properties. Thus they are generally more toxic to all forms of life than are zinc salts and for that reason may give better protection against termites. In contrast to mercury salts, they do not plate out on steel and can be used in conventional apparatus. They are too expensive to be used merely to protect against decay.

### Copper Sulphate

Copper sulphate has a low cost per unit of toxicity. It is quite poisonous to all forms of life. It is very corrosive to steel which fact greatly restricts its use. It has been used in concrete treating tanks. If its solution is made strongly ammoniacal it may be used in a steel treating cylinder. It is reported to have given good results in service, especially in the treatment of telephone poles in Europe.

### Mercuric Chloride

Mercuric chloride is even more toxic to man than copper sulphate or arsenic trioxide. It has an appreciable vapor pressure and should not be recommended as a preservative for general use. It has given some good results in service.

### Nickel Chloride

Nickel chloride has a low cost per unit of toxicity -- about the same as copper sulphate and less than mercuric chloride. It is less toxic

to man than either of those two salts and much less corrosive to steel. However, it is too corrosive to be used in a steel treating cylinder without the addition of some inhibitor, such as a bichromate. It could be used alone in the steeping process in a tank made of wood, copper, or concrete. Two hundred ties treated with a mixture of nickel sulphate and sodium bichromate have been in test since 1928. The inspection at the end of 5 years indicated no superiority of this treatment over zinc chloride or sodium fluoride. If any further tests are started on a soluble nickel salt, the chloride should be chosen as there is some evidence to show that sulphates weaken wood.

#### Sodium Chromate and Sodium Dichromate

These salts are very toxic to fungi and only moderately toxic to humans. They are cheap enough so that their costs per unit of toxicity are about the same as that of a 1:1 mixture of arsenic trioxide and sodium arsenite. Of the inorganic compounds tested only arsenic trioxide offers toxicity at a lower cost.

The toxicity of both compounds lies in the chromium which is in the hexavalent state in each. Sodium dichromate is slightly acid, whereas sodium chromate is slightly alkaline. This difference might be reflected in a difference in the tendencies of the compounds to react with constituents of the wood which, in turn, would cause a difference in permanence. For this reason service tests should include both compounds.

#### Thallium Sulphate

Because of its reputed toxicity to insects, thallium sulphate was one of the materials chosen for the termite tests being made by Hunt and Snyder. The results so far have been disappointing. It is too expensive to be used merely for protection against decay.

#### Zinc Chloride

If it were an untried preservative today, zinc chloride would appear only fairly promising. Its cost per unit of toxicity is higher than that of a number of other salts, it is somewhat corrosive to steel, and its concentrated solutions act on wood. However, it has given very good results in actual service and in comparative service tests it has proven more effective than some salts which were superior to it by laboratory tests.

#### Sodium Tetrachlorphenolate and Sodium Pentachlorphenolate

Sodium tetrachlorphenolate and sodium pentachlorphenolate compounds, both singly and as ingredients of proprietary formulae, are being promoted for use in the control of sap stain. They are worth consideration as

water-borne preservatives because they are the cheapest water-soluble toxics so far tested at the Forest Products Laboratory. They have much higher vapor pressures than do the inorganic water-soluble materials with which they would have to compete and this, combined with the fact that a smaller amount could be injected into the wood for a given cost, might result in decreased permanence. Here again service tests are needed to answer the question.

### Insoluble Compounds Formed in Wood

There are certain inorganic compounds whose solubilities are so low that they are customarily classed as insoluble, but whose molecular toxicities are so high that their saturated solutions are toxic to fungi. Outstanding examples are magnesium ammonium arsenate, basic nickel chromate, nickel ammonium phosphate, and ammoniated nickel arsenate. The low solubilities of these compounds promise high resistance to leaching as well as chemical stability and freedom from deleterious effects on glue, finishes, fastenings, and on wood itself. Although not so cheap as zinc chloride or sodium fluoride, their costs are not excessive. Because of the unique combination of their properties, they may prove useful for specific purposes, such as the treatment of mine timbers, lumber to be used in factory buildings kept at high humidities, parts of houses most subject to decay, stadium seats, highway guard rails, and sign posts. Since adequate amounts cannot be introduced in aqueous solution the compounds must be formed in wood by a double treatment. For example, the wood may be treated first with an acidic solution containing the metallic and acidic ions in chemically equivalent amounts. When this treatment is followed by a treatment with ammonia gas, the insoluble compound is deposited in the wood. Certain soluble by-products of the reaction are produced simultaneously. The nickel compounds may be injected in ammoniacal solution.<sup>4</sup>

### Magnesium Ammonium Arsenate

Magnesium ammonium arsenate is one of the rather rare inorganic compounds having a low solubility, but a sufficiently high molecular toxicity to make the saturated solution toxic to fungi. Its only possible advantage over nickel ammonium phosphate or ammoniated nickel arsenate is that in using the acid solution treatment followed by an ammonia gas treatment to form the material in wood, ordinary steel equipment can be used for the acid solution.

<sup>4</sup>

For a more complete discussion of the chemistry of these treatments see "Experiments in Fireproofing Wood (Fifth Progress Report)," by T. R. Truax, C. A. Harrison, and R. H. Baechler. Proc. A.W.P.A., 1935, p. 231-45. (Same FPL Mimeograph R1118.)

### Basic Nickel Chromate

Basic nickel chromate is deposited when ammonia evaporates from an ammoniacal solution of nickel chromate. It is toxic in spite of its low solubility. The composition of basic nickel chromate is rather indefinite and its resistance to hydrolysis not altogether certain. It warrants study in the laboratory to determine its probable value in practice.

### Nickel Ammonium Phosphate

Nickel ammonium phosphate is soluble in ammonium hydroxide and in dilute acids and could therefore be introduced into wood by either of the two methods described. Its solubility is very low, but sufficient to make it toxic to fungi. In the course of a study of the permanence of certain fire retardants, strips of wood treated with nickel ammonium phosphate by the acid and ammonia gas method were kept submerged in running water for several weeks after which the wood was analyzed. It was found that, within experimental error, no nickel had leached from the wood and a chemically equivalent amount of phosphate had been likewise retained. In similar pieces of wood treated with diammonium phosphate it was found that practically all the salt had been leached out.

Nickel ammonium phosphate is cheaper than ammoniated nickel arsenate and safer to use. It would be expected to be less effective against decay and especially against termites, but nevertheless should be considered as a possible protection against both of these wood destroyers. When used in fairly large amounts, both compounds reduce the combustibility of wood, but this effect is unimportant in the range of salt retention ordinarily used in wood preservation.

### Ammoniated Nickel Arsenate

Ammoniated nickel arsenate is a term used loosely here to cover the material precipitated when ammonia is added to a solution containing nickel and arsenate ions. Its composition varies with conditions of formation, but of the samples made in this Laboratory under varied conditions, all were found to be toxic. Soluble arsenic compounds have not proven very effective in the international termite exposure test conducted by Hunt and Snyder, but this nonleaching arsenate may be an exception. The danger of the action of molds that produce arsenical gases is minimized by the presence of nickel in the molecule which would more than double the potential toxicity against fungi. This is the only material now known that one could suggest as a treatment to give to wood, which is to be painted, relatively permanent protection against fungi, insects, and fire under conditions favoring leaching. More laboratory work on it is desirable, but enough is known to warrant its inclusion both in the next tests started in the termite study and in the next service tests started on treated ties.

## Conclusions

Service tests are indicated for the following chemicals dissolved in gas oil: tetrachlorphenol, pentachlorphenol, dinitrochlorbenzene, a mixture of 11 percent naphthalene plus 2 percent tetrachlorphenol in gas oil, and a mixture of 11 percent naphthalene plus 2 percent pentachlorphenol in gas oil.

The following chemicals should be dissolved in Stoddard solvent and put into test: tetrachlorphenol, pentachlorphenol, dichloralphanaphthol, naphthalene, alphachloronaphthalene, trichlorbenzene, dinitrochlorbenzene, orthophenylphenol, monochlor ortho phenylphenol, betanaphthol (with the addition of 10 percent pine oil to the solvent), 1-chlorbetanaphthol, nitrotoluene, a 1:1 mixture of naphthalene and diphenyl, and a 1:1 mixture of naphthalene and acenaphthene.

The following water-soluble chemicals should be put into test: sodium chromate, sodium dichromate, a 1:1 mixture of boric acid and borax, sodium tetrachlorphenolate, sodium pentachlorphenolate, nickel chloride, and dinitrophenol.

Termite exposure tests as well as the usual service tests should be started on wood impregnated with magnesium ammonium arsenate, basic nickel chromate, nickel ammonium phosphate, and ammoniated nickel arsenate.

Strong solutions of zinc acetate, boric acid-borax, and sodium chromate are recommended for the steeping treatment of greenposts and ties to be put into service tests. A steeping treatment followed by seasoning and then a pressure treatment with gas oil should be investigated.