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EXPERIMENTS IN FIREPROOFING WOOD

Fourth Progress Report

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and
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Assistant Chemist



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EXPERIMENTS IN FIREPROOFING WOOD--FOURTH PROGRESS REPORT*

By

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The last three annual meetings of the American Wood-Preservers' Association have received reports of the continued studies, made at the Forest Products Laboratory, in the fire-retardant properties of various chemicals when impregnated into wood. Up to the present the reports have dealt almost entirely with the effectiveness of single chemicals. Although the work on single chemicals has been continued to some extent, during the past year more attention has been given to combinations of chemicals.

The 1932 report summarized the results of preliminary tests on 61 single chemicals and more intensive tests on 7 single chemicals and one mixture of chemicals. The present report describes the results of preliminary tests on 6 additional single chemicals and 34 combinations of chemicals, and more intensive tests on 7 combinations.

The general method of treating wood and testing it for fire resistance that was described in detail in the 1930 and 1931 papers has been followed throughout; thus the results obtained from year to year are comparable. In preliminary or extensive surveys the test specimens are cut from southern yellow pine boards before treatment, impregnated with the chemical solutions under pressure, dried, and tested without resurfacing. The specimens are treated with two concentrations of solutions of each chemical, intended to give absorptions of approximately 1 pound and 5 pounds, respectively, of anhydrous chemical per cubic foot of wood. In intensive surveys the wood is treated in board form with five concentrations of each chemical, intended to give absorptions of about 1, 2, 3, 5, and 7 to 8 pounds, respectively, of anhydrous chemical per cubic foot of wood. The boards are redried, surfaced lightly to uniform thickness, and cut into test specimens. In both series the test specimens are conditioned to approximately constant weight under controlled atmospheric conditions

*Presented at the Twenty-Ninth annual meeting of the American Wood-Preservers' Association held at the Hotel Sherman, Chicago, Ill., on January 24, 25, 26, 1933.

that bring untreated wood to a moisture content of 6 to 7 percent. Moisture-content determinations are made on samples cut immediately before the fire tests.

The fire-tube test¹ has been used as the measure of fire resistance in both series. In this test loss in weight of the specimen and temperature at the top of the fire tube are the principal measures of fire resistance. Since readings of both conditions are taken at regular intervals the rate of burning, as well as the total loss in weight and maximum temperature, can be computed. Observations are also made on the tendency of the specimens to glow after the flame dies out.

Extensive Survey

Single Chemicals

Six additional single chemicals, namely, calcium arsenate, monobasic magnesium phosphate, monobasic zinc phosphate, monobasic sodium phosphate, dibasic sodium phosphate, and dextrose, have been tested during the past year, bringing the present total to 67. The results obtained with these 6 chemicals are shown in Table 1, and those obtained with 5 other previously reported chemicals, representing a wide range of effectiveness in reducing flaming, are shown in italics for comparison.

Of the 67 individual chemicals tested up to this time only 4 have shown a high degree of effectiveness in reducing both flaming and glowing. They are diammonium phosphate, monoammonium phosphate, phosphoric acid, and monobasic magnesium phosphate. Several others, such as aluminum sulphate, ammonium bromide, and ammonium chloride, were effective in stopping combustion of both types when present in heavy absorptions, but not when in light absorptions. Something like half of the single chemicals tested have shown a distinct effect in reducing the tendency of wood to burn by flaming and a somewhat smaller number the tendency of wood to burn by glowing. In the specific compounds tested the following radicals, listed alphabetically, appear to have contributed

¹ For a description of the fire-tube test see "Fire resistance of wood treated with zinc chloride and diammonium phosphate" by Geo. M. Hunt, T. R. Truax, and C. A. Harrison in the 1930 Proc. of the Amer. Wood Preservers' Assn., pages 130 to 159.

controlled atmospheric conditions that bring untreated wood to a moisture content of 5 to 7 per cent. Moisture-content determinations are made on samples cut immediately before the fire tests.

The fire-tube test¹ has been used as the measure of fire resistance in both series. In this test loss in weight of the specimen and temperature at the top of the fire tube are the principal measures of fire resistance. Since readings of both conditions are taken at regular intervals the rate of burning, as well as the total loss in weight and maximum temperature, can be computed. Observations are also made on the tendency of the specimens to glow after the flame dies out.

Extensive Survey

Single Chemicals

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Of the 67 individual chemicals tested up to this time only 4 have shown a high degree of effectiveness in reducing both flaming and glowing. They are diammonium phosphate, monommonium phosphate, phosphoric acid, and monobasic magnesium phosphate. Several others, such as aluminum sulphate, ammonium bromide, and ammonium chloride, were effective in stopping combustion of both types when present in heavy absorptions, but not when in light absorptions. Something like half of the single chemicals tested have shown a distinct effect in reducing the tendency of wood to burn by flaming and a somewhat smaller number the tendency of wood to burn by glowing. In the specific compounds tested the following radicals, listed alphabetically, appear to have contributed substantially to fire resistance:

Basic Radicals

aluminum
ammonium
calcium
cobalt
copper
iron
magnesium
manganese
nickel
tin
zinc

Acid Radicals

arsenate or arsenite
borate
bromide
chloride
molybdate
phosphate
pyrophosphate
silicate
stannate
tungstate
vanadate

¹For a description of the fire-tube test see "Fire resistance of wood treated with chemicals," by T. R. Truax, and "Fire resistance of wood treated with chemicals," by T. R. Truax and C. A. Harrison in the 1930 Proceedings of the Amer. Wood Preservers' Assn., pages 126 to 153.

TABLE 1.—RESULTS OF TESTS ON SINGLE CHEMICALS IN EXTENSIVE SURVEY

Name of chemical ¹	Grade of chemical	Light absorption				Heavy absorption					
		Absorption per cubic foot of wood ²	Per cent	Loss in weight ³	Maximum temperature	Tendency to glow ³	Absorption per cubic foot of wood ²	Per cent	Loss in weight ³	Maximum temperature	Tendency to glow ³
Untreated wood		6.49	6.7	82.8	897	Moderate	6.49	6.7	82.8	897	Moderate
Zinc chloride (Zn Cl ₂)	Tech.	1.67	7.9	82.2	795	Moderate	5.97	11.2	17.2	135	Slight
Ammonium phosphate, monobasic (NH ₄ H ₂ PO ₄)	Tech.	1.16	6.8	89.8	739	None	5.14	7.1	17.8	165	None
Calcium arsenate, monobasic (Ca(H ₂ AsO ₄) ₂)	Tech.	1.06	7.3	74.8	843	Moderate	5.49	8.1	29.9	225	Moderate
Magnesium phosphate ⁴ , monobasic (Mg(H ₂ PO ₄) ₂)	Tech.	.94	7.8	69.8	741	None	5.92	9.7	38.2	235	None
Zinc phosphate ⁴ , monobasic (Zn(H ₂ PO ₄) ₂)	Tech.	1.09	6.1	65.8	725	Very slight	5.74	7.8	27.5	162	None
Sodium phosphate, tribasic (Na ₃ PO ₄ ·12H ₂ O)	Tech.	1.11	8.3	63.5	854	Moderate	6.19	11.6	48.5	749	Slight
Sodium chloride (Na Cl)	Tech.	2.25	8.9	79.0	839	Moderate	6.19	8.8	49.2	816	Moderate
Sodium phosphate, dibasic (Na ₂ HPO ₄ ·H ₂ O)	Tech.	1.22	7.5	77.5	779	None	6.19	7.4	69.2	741	None
Dextrose (C ₆ H ₁₂ O ₆ ·H ₂ O)	C. P.	1.15	7.7	75.0	681	Moderate	6.41	7.6	68.8	878	Moderate
Oxalic acid (H ₂ C ₂ O ₄ ·2H ₂ O)	Tech.	1.69	7.4	82.0	872	Moderate	5.48	9.2	81.8	839	Moderate
Indic acid (H ₂ C ₂ O ₄ ·3H ₂ O)	Tech.	.56	7.0	89.5	815	Moderate	5.50	17.0	55.0	735	Moderate

¹A complete list of chemicals, previously tested, was reported in the 1933 Proceedings of the Amer. Wood Preservers' Assn. for comparison.

²Figures indicate chemicals reported in the 1933 Proceedings and included here for comparison.

³Figures indicate chemicals reported in the 1933 Proceedings and included here for comparison.

⁴Loss in weight per cubic foot of wood.

⁵Loss in weight per cubic foot of wood.

⁶Loss in weight per cubic foot of wood.

⁷Loss in weight per cubic foot of wood.

⁸Loss in weight per cubic foot of wood.

⁹Loss in weight per cubic foot of wood.

¹⁰Loss in weight per cubic foot of wood.

¹¹Loss in weight per cubic foot of wood.

¹²Loss in weight per cubic foot of wood.

¹³Loss in weight per cubic foot of wood.

¹⁴Loss in weight per cubic foot of wood.

¹⁵Loss in weight per cubic foot of wood.

¹⁶Loss in weight per cubic foot of wood.

¹⁷Loss in weight per cubic foot of wood.

¹⁸Loss in weight per cubic foot of wood.

¹⁹Loss in weight per cubic foot of wood.

²⁰Loss in weight per cubic foot of wood.

²¹Loss in weight per cubic foot of wood.

²²Loss in weight per cubic foot of wood.

²³Loss in weight per cubic foot of wood.

²⁴Loss in weight per cubic foot of wood.

²⁵Loss in weight per cubic foot of wood.

²⁶Loss in weight per cubic foot of wood.

²⁷Loss in weight per cubic foot of wood.

²⁸Loss in weight per cubic foot of wood.

²⁹Loss in weight per cubic foot of wood.

³⁰Loss in weight per cubic foot of wood.

³¹Loss in weight per cubic foot of wood.

³²Loss in weight per cubic foot of wood.

³³Loss in weight per cubic foot of wood.

³⁴Loss in weight per cubic foot of wood.

³⁵Loss in weight per cubic foot of wood.

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⁴³Loss in weight per cubic foot of wood.

⁴⁴Loss in weight per cubic foot of wood.

⁴⁵Loss in weight per cubic foot of wood.

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substantially to fire resistance:

Basic Radicals	Acid Radicals
aluminum	arsenate or arsenite
ammonium	borate
calcium	bromide
cobalt	chloride
copper	molybdate
lithium	phosphate
magnesium	selenite
manganese	stannate
nickel	tungstate
tin	vanadate
zinc	

Analysis of the data on the various chemicals tested indicates that no single compound is an ideal fire retardant. None of the single chemicals tested appear to possess in combination a high degree of fire resistance, low cost, resistance to leaching, and freedom from objectionable features, such as corrosion of metals, interference with gluing and finishing, and injury to the strength and other desirable properties of the wood. The ammonium phosphates in concentrations great enough to give a high degree of fire resistance, for example, add too much to the cost of wood for most uses, interfere to some extent with gluing, are somewhat corrosive to metals, and leach easily. Apparently, cheap, effective, permanent treatments that are not injurious to the wood nor objectionable in use can most easily be found in combinations of chemicals. Most of our work during the past year has been in this field.

Combinations of Chemicals

The specific aims in working with combinations of chemicals are:

1. To find, if possible, treatments that bring greater fire resistance.
2. To reduce the cost of treatment.
3. To develop treatments that do not injure the wood nor impart objectionable properties to it.
4. To develop a treatment resistant to leaching.
5. To find a treatment that combines fire resistance, decay resistance, and nonleaching properties.

Of the possible combinations of the most effective radicals, ammonium arsenate, ammonium borate, and diammonium and monoammonium phosphates were tested and reported upon in the 1932 report to this Association. The ammonium phosphates are among the most effective single chemicals thus far tested. Ammonium arsenate and ammonium borate, while

unusually effective, are somewhat less so than might be expected. Some work has also been done on zinc borate, showing that it has considerable fire resistance.²

Many of the combinations of the more effective radicals produce compounds that are highly insoluble in water. For example, the dibasic and tribasic phosphates of magnesium (MgHPO_4 and $\text{Mg}_3(\text{PO}_4)_2$) and of zinc (ZnHPO_4 and $\text{Zn}_3(\text{PO}_4)_2$) are very low in solubility. The same is true of the arsenates of magnesium and zinc. Double phosphates and arsenates of magnesium and ammonium (MgNH_4PO_4 and $\text{MgNH}_4\text{AsO}_4$) or of zinc and ammonium (ZnNH_4PO_4 and $\text{ZnNH}_4\text{AsO}_4$) also have this same characteristic. These low-solubility compounds are obviously not suitable for treating wood directly, although they may be formed in wood by indirect methods. The monobasic or primary forms of phosphates and arsenates, however, are sufficiently soluble in water to make them practical from the standpoint of wood impregnation and they may serve as the first step in the production in the wood of compounds of low solubility.

The 34 combinations of chemicals studied are included in Table 2. Some of the treatments were made in a single impregnation by combining the chemicals in the treating solution. In others an absorption of solution was followed by an ammonia-gas treatment. In still others the wood was impregnated with one solution, dried, and then reimpregnated with a second solution.

The first effort to utilize combinations of the more effective acid and basic radicals that are usually insoluble in water consisted in forming low-solubility compounds in the wood by treatments involving two solutions. Treatments No. 15, 16, and 17 (Table 2) were made in this way. In treatment No. 16 the wood was first impregnated with a solution of an aluminum chloride, dried, and then reimpregnated with a solution of trisodium phosphate. When a solution of an aluminum salt is mixed with a solution of a tribasic phosphate, a precipitate of aluminum phosphate forms. The composition of the precipitate, that is, the ratio of Al_2O_3 and P_2O_5 , depends upon the temperature, concentration, and reaction of the solution. For convenience it is assumed in Table 2 that in this treatment the products formed in the wood were neutral aluminum phosphate (AlPO_4), a compound of very low solubility, and sodium chloride (NaCl). Likewise, in treatment No. 17 the separate impregnations with barium chloride and sodium sulphate theoretically formed barium sulphate (BaSO_4), also highly insoluble, and sodium chloride; in treatment No. 15 zinc chloride and sodium stannate were used separately to form zinc stannate (ZnSnO_3) and sodium chloride.

²Tests on the inflammability of untreated wood and of wood treated with fire-retarding compounds by R. E. Prince, National Fire Protection Association Proceedings (1915), illus.

TABLE 2.—RESULTS OF TESTS ON COMBINATIONS OF CHEMICALS IN EXTENSIVE SURVEY

Treatment No.	Chemicals used in treatments		Chemicals theoretically formed in the wood ¹		Test results for light and heavy treatments					
	Name and formula	Percentage of total anhydrous chemical	Name and formula	Percentage of total anhydrous chemical	Absorption of anhydrous chemicals		Apparent moisture content ²	Results of tests in the fire tube		
					Per cubic foot	Per 100 lbs. of air-dry wood		Loss in weight ³	Maximum temperature	Tendency to glow ⁴
		Per cent		Per cent	Pounds	Pounds	Per cent	Per cent	Deg. C.	
1A	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Phosphoric acid (H_3PO_4) Microcosmic salt ($NaNH_4HPO_4$)	25.41 38.31 36.3	Extent of chemical reaction unknown		2.96 15.43	8.62 44.00	10.6 9.6	62.8 13.5	682 185	Very slight None
1B	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Phosphoric acid (H_3PO_4) Microcosmic salt ($NaNH_4HPO_4$) Ammonia gas (NH_3) on wet wood	21.3 32.6 30.6 15.6	Magnesium ammonium phosphate ($MgNH_4PO_4$) Sodium chloride ($NaCl$) Ammonium chloride (NH_4Cl) Diammonium phosphate ($(NH_4)_2HPO_4$)	30.9 13.1 12.0 44.0	3.49 18.18 18.18 44.0	10.16 51.90	8.3 7.9	21.2 10.8	209 168	Very slight None
1C	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Phosphoric acid (H_3PO_4) Microcosmic salt ($NaNH_4HPO_4$) Ammonia gas (NH_3) on dry wood	21.3 32.6 30.6 15.6	Magnesium ammonium phosphate ($MgNH_4PO_4$) Sodium chloride ($NaCl$) Ammonium chloride (NH_4Cl) Diammonium phosphate ($(NH_4)_2HPO_4$)	30.9 13.1 12.0 44.0	3.49 18.18 18.18 44.0	10.16 51.90	7.9 8.1	21.2 10.2	211 166	Very slight None
2A	Magnesium phosphate, dibasic ($MgHPO_4 \cdot 3H_2O$) Phosphoric acid (H_3PO_4)	55.1 44.9	Magnesium phosphate, monobasic (MgH_2PO_4)	100.0	4.81 12.76	2.42 12.76	7.8 9.5	72.0 25.8	761 268	None Very slight
2B	Magnesium phosphate, dibasic ($MgHPO_4 \cdot 3H_2O$) Phosphoric acid (H_3PO_4) Ammonia gas (NH_3) on wet wood	44.7 36.4 18.9	Magnesium ammonium phosphate ($MgNH_4PO_4$) Ammonium phosphate, dibasic ($(NH_4)_2HPO_4$)	51.1 48.9	1.00 5.32	2.99 15.73	8.3 7.8	69.0 16.8	637 187	Very slight None
2C	Magnesium phosphate, dibasic ($MgHPO_4 \cdot 3H_2O$) Phosphoric acid (H_3PO_4) Ammonia gas (NH_3) on dry wood	44.7 36.4 18.9	Magnesium ammonium phosphate ($MgNH_4PO_4$) Ammonium phosphate, dibasic ($(NH_4)_2HPO_4$)	51.1 48.9	1.00 5.32	2.99 15.73	7.5 7.8	74.2 19.2	749 196	None None
3A	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Sodium phosphate, dibasic ($Na_2HPO_4 \cdot 12H_2O$) Phosphoric acid (H_3PO_4)	44.2 32.9 22.9	Extent of chemical reaction unknown		1.77 9.54	5.44 29.48	10.3 17.4	72.8 28.2	767 227	Moderate Very slight
3B	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Sodium phosphate, dibasic ($Na_2HPO_4 \cdot 12H_2O$) Phosphoric acid (H_3PO_4) Ammonia gas (NH_3) on wet wood	36.2 28.4 19.8 13.6	Magnesium ammonium phosphate ($MgNH_4PO_4$) Sodium chloride ($NaCl$) Ammonium chloride (NH_4Cl)	55.1 23.5 21.4	2.05 11.05	6.29 34.13	10.0 8.6	41.5 14.0	479 167	Very slight None
3C	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Sodium phosphate, dibasic ($Na_2HPO_4 \cdot 12H_2O$) Phosphoric acid (H_3PO_4) Ammonia gas (NH_3) on dry wood	36.2 28.4 19.8 13.6	Magnesium ammonium phosphate ($MgNH_4PO_4$) Sodium chloride ($NaCl$) Ammonium chloride (NH_4Cl)	55.1 23.5 21.4	2.05 11.05	6.29 34.13	7.2 6.5	51.8 14.2	637 180	Slight Very slight
4A	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Ammonium phosphate, monobasic ($NH_4H_2PO_4$)	45.2 54.8	Extent of chemical reaction unknown		1.58 8.42	4.68 22.78	10.2 17.0	72.2 15.8	763 161	None None
4B	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Ammonium phosphate, monobasic ($NH_4H_2PO_4$) Ammonia gas (NH_3) on wet wood	38.9 47.2 13.9	Magnesium ammonium phosphate ($MgNH_4PO_4$) Ammonium chloride (NH_4Cl)	55.2 43.8	1.83 9.79	5.44 26.45	9.0 12.7	58.8 16.2	789 178	Very slight None
4C	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Ammonium phosphate, monobasic ($NH_4H_2PO_4$) Ammonia gas (NH_3) on dry wood	38.9 47.2 13.9	Magnesium ammonium phosphate ($MgNH_4PO_4$) Ammonium chloride (NH_4Cl)	55.2 43.8	1.83 9.79	5.44 26.45	7.5 8.5	59.8 14.8	607 168	None None
5A	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Sodium phosphate, monobasic ($NaH_2PO_4 \cdot H_2O$)	44.2 55.8	Extent of chemical reaction unknown		1.40 9.90	3.48 24.42	8.3 9.5	74.5 34.8	835 342	Moderate Slight
5B	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Sodium phosphate, monobasic ($NaH_2PO_4 \cdot H_2O$) Ammonia gas (NH_3) on wet wood	36.2 48.2 13.6	Magnesium ammonium phosphate ($MgNH_4PO_4$) Sodium chloride ($NaCl$) Ammonium chloride (NH_4Cl)	55.1 23.5 21.4	1.62 11.43	4.03 29.04	7.2 7.3	62.6 15.6	800 290	Slight Very slight
5C	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Sodium phosphate, monobasic ($NaH_2PO_4 \cdot H_2O$) Ammonia gas (NH_3) on dry wood	36.2 48.2 13.6	Magnesium ammonium phosphate ($MgNH_4PO_4$) Sodium chloride ($NaCl$) Ammonium chloride (NH_4Cl)	55.1 23.5 21.4	1.62 11.43	4.03 29.04	6.7 6.6	64.1 15.9	794 189	Moderate Very slight
6A	Magnesium oxide (MgO) Phosphoric acid (H_3PO_4)	17.0 83.0	Magnesium phosphate, monobasic (MgH_2PO_4)	100.0	1.06 5.72	3.04 16.38	7.8 9.7	67.5 14.5	721 187	None None
6B	Magnesium oxide (MgO) Phosphoric acid (H_3PO_4) Ammonia gas (NH_3) on wet wood	14.0 86.0 17.8	Magnesium ammonium phosphate ($MgNH_4PO_4$) Ammonium phosphate, dibasic ($(NH_4)_2HPO_4$)	61.0 39.0	1.31 7.06	3.74 20.18	7.0 7.8	61.8 17.8	728 178	None None
7A	Zinc chloride ($ZnCl_2$) Ammonium phosphate, monobasic ($NH_4H_2PO_4$)	56.2 43.8	Extent of chemical reaction unknown		1.43 7.83	3.56 22.17	7.8 10.2	72.5 17.1	804 192	Very slight Very slight
7B	Zinc chloride ($ZnCl_2$) Ammonium phosphate, monobasic ($NH_4H_2PO_4$) Ammonia gas (NH_3) on wet wood	47.8 49.3 11.9	Zinc ammonium phosphate ($ZnNH_4PO_4$) Ammonium chloride (NH_4Cl)	82.4 17.6	1.65 8.59	4.04 26.99	8.5 7.3	67.8 14.3	802 181	Slight Very slight
7C	Zinc chloride ($ZnCl_2$) Ammonium phosphate, monobasic ($NH_4H_2PO_4$) Ammonia gas (NH_3) on dry wood	47.8 49.3 11.9	Zinc ammonium phosphate ($ZnNH_4PO_4$) Ammonium chloride (NH_4Cl)	82.4 17.6	1.65 8.59	4.04 26.99	6.2 5.8	69.5 13.2	784 164	Very slight Very slight
8A	Zinc chloride ($ZnCl_2$) Sodium phosphate, monobasic ($NaH_2PO_4 \cdot H_2O$)	53.2 46.8	Extent of chemical reaction unknown		1.89 9.07	4.21 22.80	7.8 9.2	72.0 20.2	806 224	Moderate Very slight
8B	Zinc chloride ($ZnCl_2$) Sodium phosphate, monobasic ($NaH_2PO_4 \cdot H_2O$) Ammonia gas (NH_3) on wet wood	47.0 41.3 11.7	Zinc ammonium phosphate ($ZnNH_4PO_4$) Sodium chloride ($NaCl$) Ammonium chloride (NH_4Cl)	61.5 30.1 18.4	1.81 10.32	4.77 25.60	7.6 8.0	67.8 17.2	849 222	Slight Very slight
8C	Zinc chloride ($ZnCl_2$) Sodium phosphate, monobasic ($NaH_2PO_4 \cdot H_2O$) Ammonia gas (NH_3) on dry wood	47.0 41.3 11.7	Zinc ammonium phosphate ($ZnNH_4PO_4$) Sodium chloride ($NaCl$) Ammonium chloride (NH_4Cl)	61.5 30.1 18.4	1.81 10.32	4.77 25.60	6.6 6.5	70.0 14.5	771 188	Moderate Very slight
9A	Zinc oxide (ZnO) Phosphoric acid (H_3PO_4)	29.2 70.7	Zinc phosphate, monobasic (ZnH_2PO_4)	100.0	1.09 5.74	3.14 16.48	6.1 7.8	65.5 27.5	725 332	Very slight None
9B	Zinc oxide (ZnO) Phosphoric acid (H_3PO_4) Ammonia gas (NH_3) on wet wood	24.8 69.7 15.6	Zinc ammonium phosphate ($ZnNH_4PO_4$) Ammonium phosphate, dibasic ($(NH_4)_2HPO_4$)	57.4 42.6	1.30 6.82	3.76 19.72	6.9 7.1	60.2 14.5	721 192	None None
10	Zinc chloride ($ZnCl_2$) Sodium phosphate, dibasic ($Na_2HPO_4 \cdot 12H_2O$) Ammonium hydroxide (NH_4OH)	43.5 45.9 11.2	Zinc ammonium phosphate ($ZnNH_4PO_4$) Sodium chloride ($NaCl$) Ammonium chloride (NH_4Cl)	60.4 39.6 17.8	1.81 10.32	4.58 25.60	8.6 8.9	73.2 16.0	784 803	Moderate Very slight
11A	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Arsenic acid ($H_3AsO_4 \cdot H_2O$) Sodium arsenate, tribasic ($Na_3AsO_4 \cdot 12H_2O$) Ammonia gas (NH_3) on wet wood	28.9 29.1 42.0 9.4	Extent of chemical reaction unknown		2.40 15.45	6.97 45.00	8.2 11.0	43.6 12.0	589 183	Moderate Slight
11B	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Arsenic acid ($H_3AsO_4 \cdot H_2O$) Sodium arsenate, tribasic ($Na_3AsO_4 \cdot 12H_2O$) Ammonia gas (NH_3) on dry wood	28.1 26.3 36.2 9.4	Magnesium ammonium arsenate ($MgNH_4AsO_4$) Sodium chloride ($NaCl$) Ammonium arsenate ($NH_4H_2AsO_4$)	50.0 32.2 17.8	2.65 17.42	7.69 40.76	8.4 11.4	23.2 9.5	243 174	Moderate None
11C	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Arsenic acid ($H_3AsO_4 \cdot H_2O$) Sodium arsenate, tribasic ($Na_3AsO_4 \cdot 12H_2O$) Ammonia gas (NH_3) on dry wood	28.1 26.3 36.2 9.4	Magnesium ammonium arsenate ($MgNH_4AsO_4$) Sodium chloride ($NaCl$) Ammonium arsenate ($NH_4H_2AsO_4$)	50.0 32.2 17.8	2.65 17.42	7.69 40.76	7.2 8.9	21.5 9.8	211 168	Moderate Very slight
12A	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$)	31.6 68.4	Extent of chemical reaction unknown		1.74 9.47	4.60 24.92	8.6 10.1	46.2 22.5	668 259	Moderate Moderate
12B	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) Ammonia gas (NH_3) on wet wood	29.4 61.5 10.1	Magnesium hydroxide, $Mg(OH)_2$ Ammonium chloride (NH_4Cl) Sodium molybdate (Na_2MoO_4)	15.7 28.8 55.5	1.94 10.54	5.12 27.75	8.6 9.0	33.5 18.2	332 220	Moderate Slight
12C	Magnesium chloride ($MgCl_2 \cdot 6H_2O$) Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) Ammonia gas (NH_3) on dry wood	28.4 61.5 10.1	Magnesium hydroxide, $Mg(OH)_2$ Ammonium chloride (NH_4Cl) Sodium molybdate (Na_2MoO_4)	15.7 28.8 55.5	1.94 10.54	5.12 27.75	7.4 7.6	36.5 15.5	394 194	Slight None
13	Zinc chloride ($ZnCl_2$) Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) Ammonium hydroxide (NH_4OH)	35.7 39.2 25.1	Zinc hydroxide, $Zn(OH)_2$ Ammonium chloride (NH_4Cl) Sodium molybdate (Na_2MoO_4)	24.2 25.9 49.9	1.97 11.04	5.18 29.46	7.4 8.0	63.5 18.2	841 232	Moderate Slight
14	Zinc chloride ($ZnCl_2$) Baric acid (H_3BO_3)	52.0 48.0	Extent of chemical reaction unknown		1.37 6.31	3.41 18.38	7.4 8.0	67.0 17.8	745 177	Slight None
15	Zinc chloride ($ZnCl_2$) Sodium stannate ($Na_2SnO_3 \cdot 3H_2O$)	32.9 67.1	Zinc stannate ($ZnSnO_3$) Sodium chloride ($NaCl$) Excess sodium stannate (Na_2SnO_3)	56.1 28.3 15.6	2.37 12.38	6.62 34.90	9.3 9.3	68.0 11.0	819 119	Moderate None
	Zinc chloride ($ZnCl_2$) Sodium stannate ($Na_2SnO_3 \cdot 3H_2O$)	32.9 67.1	Zinc stannate ($ZnSnO_3$) Sodium chloride ($NaCl$) Excess sodium stannate (Na_2SnO_3)	56.2 28.4 15.4	2.37 12.38	6.62 34.90	10.1 10.1	51.0 11.0	321 119	Slight None
16	Aluminum chloride ($AlCl_3$) Sodium phosphate, tribasic ($Na_3PO_4 \cdot 12H_2O$)	51.1 48.9	Aluminum phosphate ($AlPO_4$) Sodium chloride ($NaCl$) Excess aluminum chloride ($AlCl_3$)	36.5 52.0 11.5	2.27 10.54	7.61 27.75	8.2 9.0	62.5 18.2	822 220	Moderate Slight
	Aluminum chloride ($AlCl_3$) Sodium phosphate, tribasic ($Na_3PO_4 \cdot 12H_2O$)	63.8 36.2	Aluminum phosphate ($AlPO_4$) Sodium chloride ($NaCl$) Excess aluminum chloride ($AlCl_3$)	26.9 54.3 18.8	9.99 26.08	26.08 11.5	11.5 11.5	41.6 18.2	475 220	Moderate Slight
17	Barium chloride ($BaCl_2 \cdot 2H_2O$) Sodium sulphate ($Na_2SO_4 \cdot 10H_2O$)	56.7 44.3	Barium sulphate ($BaSO_4$) Sodium chloride ($NaCl$) Excess sodium sulphate (Na_2SO_4)	62.2 31.2 6.6	2.88 12.38	6.93 34.90	7.0 7.0	69.8 11.0	863 119	Moderate None
	Barium chloride ($BaCl_2 \cdot 2H_2O$) Sodium sulphate ($Na_2SO_4 \cdot 10H_2O$)	59.3 40.7	Barium sulphate ($BaSO_4$) Sodium chloride ($NaCl$) Excess barium chloride ($BaCl_2$)	60.5 25.3 14.2	7.32 12.38	22.35 34.90	7.3 7.3	62.0 11.0	846 119	Moderate None

¹ It is assumed that there was no selective absorption of chemicals by the wood and that they were present in the same proportions as in the treating solutions. In the heavy absorptions of treatments Nos. 5A, 5B, and 5C a small excess of monosodium phosphate was used in error, in the heavy absorption of treatments 11A, 11B, and 11C a small excess of arsenic acid was required to get a clear solution, and in the light absorption of treatment 12 a larger amount of ammonium hydroxide was used than shown. Hence the percentages of chemicals used and formed would vary slightly from those given.

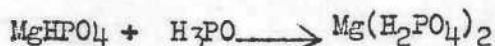
² Based on the weight of the treated wood after drying at 215° F. to 220° F. for 24 hours.

³ When the flaming stopped.

⁴ Based on untreated wood as "moderate".

Treatments Nos. 2A, 6A and 9A involved the use of two chemicals each but formed single chemical compounds and are also reported in Table 1 under single chemicals. For a discussion of the chemical reaction see the text under "Molybdate treatment".

The second general method of attack, using compounds of the more effective radicals, involved the primary or monobasic form of phosphate, arsenate, and so forth of various basic elements. Several treatments were made involving this principle. Since the monobasic form of these compounds is either not readily available in technical grade or is expensive, most of the treatments were made with other chemicals that produced the soluble monobasic form. In treatment No. 2 of Table 2, for example, dibasic magnesium phosphate was dissolved in phosphoric acid, giving monobasic magnesium phosphate as follows:



A similar result was obtained more advantageously in treatment No. 6 of Table 2 by using magnesium oxide and phosphoric acid. The reaction theoretically produced soluble monobasic magnesium phosphate.

Several other solutions containing the magnesium and phosphate ions were used. Magnesium chloride served as the source of magnesium in making combinations with various phosphates in treatments No. 1, 3, 4, and 5 of Table 2. When a solution of magnesium chloride is mixed with a solution of a monobasic phosphate, the resulting mixture remains clear, since only soluble products are formed by the reaction:



The four compounds are in chemical equilibrium in the treating solution and in the treated wood. The most volatile of the four is ammonium chloride, and the reaction would therefore tend to go to completion as this compound volatilizes, a process that would be slow at ordinary temperatures but faster at dry-kiln temperatures.

When sodium phosphate was used (treatments No. 3 and 5 of Table 2) in place of monoammonium phosphate, sodium chloride replaced a chemically equivalent amount of ammonium chloride in the products of reaction. In treatment No. 1 microcosmic salt ($\text{NH}_4\text{NaHPO}_4$) and phosphoric acid were used instead of monoammonium phosphate and half of the ammonium chloride that would have resulted was thus replaced by sodium chloride.

Similar chemical reactions occur when zinc compounds are used in place of magnesium compounds, giving soluble monobasic zinc hydrogen phosphate. Zinc chloride and monoammonium phosphate were combined in treatment No. 7 of Table 2, zinc oxide and phosphoric acid in No. 9, and zinc chloride and monosodium phosphate in No. 8.

The chemistry of arsenic acid and the arsenates is similar to the chemistry of phosphoric acid and the phosphates. Following the same general procedure as with the phosphates, treatment No. 11 of Table 2 was made, using trisodium arsenate, arsenic acid, and magnesium chloride, producing thereby primary magnesium arsenate and sodium chloride, which are soluble.

Ammonia-Gas Treatments

A number of the treatments, involving a combination of chemicals in one solution, were followed by a treatment with ammonia gas. The purposes of the ammonia-gas treatment were to produce in the wood certain chemical compounds of low solubility that would be resistant to leaching, to reduce the acidity of the treated wood, and to increase the total fire-retardant effect by the chemical fixation of ammonia.

In most of the treatments involving the use of ammonia gas a part of the wood, previously impregnated with chemicals, was treated with the gas while still wet and a second part was dried and then so treated. A third part was tested without the gas treatment. In treatments No. 6 and 9 of Table 2 only the wet wood received the gas. The general procedure followed in the ammonia-gas treatments was as follows: The wood, previously impregnated with chemicals, was placed in a treating cylinder. Steam was applied until the temperature in the cylinder reached about 185° F. Liquid ammonia was then released into the cylinder until a pressure of 15 pounds per square inch was attained. This approximate pressure and temperature were maintained for about 12 hours, after which both the steam and the liquid ammonia were turned off. The charge was released at the end of 24 hours.

The action of the ammonia gas was similar in all treatments in which the phosphate or arsenate radical was present with either magnesium or zinc. (Treatment No. 1 to 9 and 11 of Table 2.) In these treatments there were formed insoluble compounds in which ammonium and the divalent metal were combined with a trivalent acid radical, such for example as magnesium ammonium arsenate, zinc ammonium phosphate, and so forth. In addition to the insoluble compound there were formed by-products, which varied according to the compounds used in the initial treatment of the wood. When the wood was treated with monobasic magnesium phosphate, formed by the action of phosphoric acid on either magnesium oxide or dibasic magnesium phosphate, the ammonia-gas treatment produced magnesium ammonium phosphate and diammonium phosphate according to the reaction:



When the source of magnesium was magnesium chloride, the reaction products included some soluble chloride, and when sodium phosphate constituted the source of phosphate, a soluble sodium salt was formed. Thus in treatment No. 5 of Table 2, which involved the use of both magnesium chloride and monosodium phosphate, the reaction was as follows:



A study of the reactions involved will show that the ammonia used is in excess of the amount required to form the insoluble double phosphate. Accordingly the formation of the double phosphate or arsenate is always accompanied by the formation of the ammonium salt of the solubilizing acid in the treating solution.

Zinc Ammonium Phosphate in Ammonium Hydroxide

Zinc ammonium phosphate differs from magnesium ammonium phosphate in that it is soluble in an excess of ammonium hydroxide. When a zinc chloride solution is added to a solution of a phosphate containing sufficient ammonium hydroxide, no precipitate forms at once. If the solution is allowed to stand, however, ammonia evaporates from it and a precipitate of zinc ammonium phosphate forms. This phenomenon was made the basis of treatment No. 10 of Table 2. The wood was treated with a solution containing the proper proportions of zinc chloride and disodium phosphate and enough ammonium hydroxide to keep the liquid clear. It was expected that, during the seasoning of the treated wood, ammonia would escape and zinc ammonium phosphate would be precipitated in the wood.

In making the treatment the wood was placed in a pan and covered with the treating solution. A vacuum was then created, followed by the application of pressure. At the time of the treatment the assumption was made that the wood was impregnated with a solution of the desired concentration. It now seems probable, however, that drawing the vacuum reduced the amount of ammonia in the solution to the point where zinc ammonium phosphate was precipitated in the solution and that the absorption of anhydrous chemical by the wood was less than the amount calculated. The treatment will receive further attention.

Molybdate Treatments

In treatment No. 12 of Table 2 the solution contained magnesium chloride and sodium molybdate. This was followed by a treatment with ammonia gas. In treatment No. 13 the solubility of zinc salts in ammonium hydroxide was utilized as in treatment No. 10 and a single treatment was made with a solution containing zinc chloride, sodium molybdate, and an excess of ammonium hydroxide. No reference was found in the literature to the reaction between sodium molybdate, ammonia, and the chloride of either zinc or magnesium. Some basic molybdate may be formed. Pending an experimental study of the reactions the theoretical amount of ammonia chemically fixed in the wood has been calculated on the basis of the reaction between ammonium hydroxide and the metallic chloride to form ammonium chloride and the hydroxide of the metal. (Treatments No. 12 and 13, Table 2.)

Summary of Combination Treatments in the Extensive Survey

In Table 2 are shown the kind and quantity of chemicals used in each treatment, probable compounds formed and their proportions, absorptions of total anhydrous chemical, and results obtained in fire tests. The absorptions of total chemicals in a number of the treatments were unusually large, since the aim was to obtain about 1 and 5 pounds per cubic foot, respectively, of the principal compound in each treatment. In other treatments the absorption of all chemicals approximated 1 and 5 pounds per cubic foot. To make comparison of the effectiveness of the various treatments easier the losses in weight of all treatments are plotted in Figure 1

against absorption of total chemical. The curve for diammonium phosphate is placed on the graph for comparative purposes. It is apparent that the majority of the treatments compare reasonably well with diammonium phosphate in effectiveness. Few treatments, however, can be considered as effective as the ammonium phosphates (monobasic or dibasic), pound for pound of total chemical used.

In the extensive survey of combinations of chemicals it has been impossible to arrive at a clear-cut classification of the various treatments. However, taking into consideration the quantity of chemicals used and the effect of the various combinations of chemicals on the tendency of the treated wood to flame and to glow the following comments seem justified.

Magnesium Phosphate Treatments

The treatments that resulted in the formation of magnesium phosphates with or without ammonium compounds in the wood were especially effective in stopping both flaming and glowing. These treatments involved the following combinations of chemicals: magnesium oxide and phosphoric acid with and without ammonia gas; dibasic magnesium phosphate and phosphoric acid with and without ammonia gas; magnesium chloride, microcosmic salt, and phosphoric acid with and without ammonia gas; and magnesium chloride and monoammonium phosphate with and without ammonia gas (treatments No. 6A, 6B, 2A, 2B, 2C, 1A, 1B, 1C, 4A, 4B, and 4C of Table 2). The use of chemicals yielding considerable quantities of sodium compounds in the wood along with magnesium and ammonium phosphates reduced the effectiveness of the treatments somewhat (No. 3A, 3B, 3C, 5A, 5B, and 5C). In general, final ammonia-gas treatments on either the wet or the dry wood increased the effectiveness of the earlier treatments.

Zinc Phosphate Treatments

Treatments that produced phosphates of zinc were somewhat less effective than similar magnesium phosphate treatments. Of the zinc phosphate treatments, zinc oxide and phosphoric acid with ammonia gas and zinc chloride and monoammonium phosphate with and without ammonia gas were the most effective (No. 9B, 7A, 7B, and 7C of Table 2.) Again the use of chemicals yielding sodium compounds reduced the effectiveness (No. 8A, 8B, and 8C of Table 2) and the use of ammonia gas increased the effectiveness of the treatments concerned. The treatment involving the use of zinc chloride, disodium phosphate, and ammonium hydroxide (No. 10) showed only a small degree of effectiveness although, as already explained, it now seems doubtful that the results obtained are an accurate indication of the true effectiveness.

Miscellaneous Treatments

The use of magnesium chloride, trisodium arsenate, and arsenic acid both with and without ammonia gas was highly effective in stopping flaming. Without the ammonia gas, however, the treatment had comparatively little effect on the tendency of the wood to glow (No. 11A, 11B, and 11C of Table 2.)

The treatments involving the use of a molybdate (No. 12A, 12B, 12C, and 13 of Table 2) were highly effective in reducing flaming but had a comparatively small effectiveness on glowing, though the use of ammonia gas on the wet treated wood did increase somewhat the resistance to glowing.

The combination of zinc chloride and boric acid (treatment No. 14 of Table 2) was effective in stopping both flaming and glowing, though not so outstanding as some of the other treatments.

None of the three treatments involving two solutions (No. 15, 16, and 17 of Table 2) were outstanding in their effectiveness. The zinc chloride-sodium stannate treatment was moderately effective in reducing flaming but had little effect on glowing. The other two treatments were relatively ineffective in stopping either flaming or glowing.

Intensive Survey

Certain combinations of chemicals, used in the extensive survey, appear to offer sufficient promise to warrant more intensive study. Compared with single chemicals a number of the combinations appear to possess one or more advantages such as a reduction of cost, elimination of objectionable properties of the wood in use, and a combination of fire resistance with decay resistance and slow leaching properties.

Borax-Monoammonium Phosphate

A combination of borax and monoammonium phosphate appears to offer possibilities in reducing the cost of treatment, in eliminating certain objectionable properties of the treated wood, and in adding a certain degree of decay resistance to the wood. Although the cost of monoammonium phosphate has been substantially reduced in recent years there is still the possibility of producing a cheaper treatment by the use of a certain amount of borax or other cheaper chemical in combination with the ammonium phosphate. Preliminary tests were therefore made to determine the proportion of borax and monoammonium phosphate that would show good effectiveness in stopping both flaming and glowing. The results of those tests, included in the 1932 report to this Association, indicated that a mixture of 70 parts of borax and 30 parts monoammonium phosphate (based on anhydrous chemical) was effective in stopping both flaming and glowing with an absorption of 5 to 6 pounds of anhydrous chemical per cubic foot of wood. Higher relative proportions of the borax in this approximate absorption were not so effective in stopping glowing.

A series of tests on five absorptions, ranging from approximately 1 to 8 pounds of anhydrous chemical per cubic foot of wood, was then made using a ratio of 2 parts of borax to 1 part of monoammonium phosphate. The results of the tests are shown in Table 3 and are plotted in Figure 2 in comparison with diammonium phosphate. The combination was effective, especially in the higher absorptions; the treatments were not only effective in stopping flaming and glowing but added little excess moisture to the wood.

A mixture of the two chemicals obviously gives a treatment that is less alkaline than the borax and less acid than the monoammonium phosphate and hence is freer from objectionable characteristics than either chemical alone. The best proportion of the two chemicals from a neutrality standpoint, however, has not been determined, though some work has been started along this line. In the first place the ideal degree of acidity or alkalinity, considered from all viewpoints, is not known. The question is further complicated by the fact that the proportions of the two chemicals that give a neutral reaction vary with temperature, with different concentrations of solution, and in the seasoned wood with moisture content. Preliminary tests indicate that a 12-1/2 percent solution containing 55 parts of monoammonium phosphate and 45 parts of borax is approximately neutral, but these proportions in other strengths of solution or in dry wood would not be neutral. Some further work is necessary before definite proportions of the chemicals can be recommended.

Borax in sufficient concentrations is toxic to wood destroying fungi.³ In the relatively large absorptions necessary to obtain a high degree of effectiveness as a fire retardant the borax-monoammonium phosphate treatment should give protection against decay as well as fire. The protection would not be permanent under conditions favoring leaching, however, because of the solubility of both chemicals.

Magnesium Phosphate Treatments

Four combinations of chemicals, used in the extensive survey and involving the use of magnesium and phosphate radicals, were selected for more intensive study. They were magnesium chloride and monoammonium phosphate with and without ammonia-gas treatment and magnesium chloride and monosodium phosphate with and without ammonia-gas treatment.

The two salts of each treatment were combined in amounts proportional to their molecular weights. With the ammonia-gas treatments it was necessary to use an excess of ammonia to make certain that the chemical reaction was complete. The proportion of the chemicals used in the treating

³Some experiments on the toxicity of some inorganic salts by E. Bateman and R. H. Baechler, American Wood Preservers' Association, 1927 Proceedings, pages 41 to 46.

TABLE 3.—RESULTS OF TESTS ON COMBINATIONS OF CHEMICALS IN INTENSIVE SURVEY

Chemicals used in treatment		Compounds theoretically formed in the wood			Absorption of total anhydrous chemicals ¹		Results of tests				
Name and formula	Percentage of total anhydrous chemicals	Name and formula	Percentage of total anhydrous chemicals	Per cubic foot	Per 100 lbs. of air-dry wood	Apparent moisture content ²	Loss in weight ³	Rate of loss in weight ⁴	Maximum temperature	Rate of temperature increase	Tendency to glow ⁵
	Per cent		Per cent	Pounds	Pounds	Per cent	Per cent	Per cent per minute	Degree C.	Degree C. per minute	
Borax (Na ₂ B ₄ O ₇ ·10H ₂ O)-----	67	No chemical reaction assumed-----		1.09	2.97	6.5	68.6	15.78	784	228	Very slight
Ammonium phosphate, monobasic (NH ₄ H ₂ PO ₄)-----	33			2.20	6.04	7.6	52.9	11.22	637	164	Very slight
				3.41	9.42	9.0	27.2	6.80	259	85	None
				5.69	15.71	7.7	16.5	4.12	188	81	None
				8.49	23.60	7.7	14.6	3.65	181	65	None
Magnesium chloride (MgCl ₂ ·6H ₂ O)-----	44.2	Extent of chemical reaction unknown-----		1.14	3.26	6.8	76.9	20.42	814	263	Moderate
Sodium phosphate, monobasic (NaH ₂ PO ₄ ·H ₂ O)-----	55.8			2.34	6.95	8.9	73.3	18.10	772	274	Moderate
				3.67	10.37	8.9	70.2	14.73	771	235	Slight
				5.78	16.38		64.2	10.53	562	157	Very slight
				8.83	25.15	12.6	33.2	6.38	286	70	Very slight
Magnesium chloride (MgCl ₂ ·6H ₂ O)-----	38.2	Magnesium ammonium phosphate (MgNH ₄ PO ₄)-----	55.1	1.32	3.69	7.3	66.4	16.54	823	263	Slight
Sodium phosphate, monobasic (NaH ₂ PO ₄ ·H ₂ O)-----	43.8	Sodium chloride (NaCl)-----	23.5	2.64	7.60	8.6	54.9	12.03	644	177	None
Ammonia gas (NH ₃)-----	13.6	Ammonium chloride (NH ₄ Cl)-----	21.4	4.01	11.37	11.7	27.4	6.85	264	89	None
				6.86	19.19	11.9	19.4	4.05	196	73	None
				10.09	27.84	11.9	16.2	4.05	173	62	None
Magnesium chloride (MgCl ₂ ·6H ₂ O)-----	45.2	Extent of chemical reaction unknown-----		1.09	2.99	8.0	77.1	16.87	767	243	None
Ammonium phosphate, monobasic (NH ₄ H ₂ PO ₄)-----	54.8			2.19	6.03	8.4	72.0	15.36	760	218	None
				3.19	8.78		67.8	12.63	732	185	None
				5.85	16.37	14.5	21.1	5.28	199	74	None
				8.39	24.36	14.7	17.4	4.34	176	55	None
Magnesium chloride (MgCl ₂ ·6H ₂ O)-----	38.9	Magnesium ammonium phosphate (MgNH ₄ PO ₄)-----	56.2	1.24	3.36	8.2	71.4	15.40	735	200	Very slight
Ammonium phosphate, monobasic (NH ₄ H ₂ PO ₄)-----	47.2	Ammonium chloride (NH ₄ Cl)-----	43.8	2.61	7.27	9.4	52.6	11.21	532	136	None
Ammonia gas (NH ₃)-----	13.9			3.88	10.86	10.4	22.5	5.62	224	78	None
				6.63	17.61	11.1	16.6	4.15	180	55	None
				9.86	27.05	11.9	15.6	3.90	175	53	None
Zinc chloride (ZnCl ₂)-----	54.2	Extent of chemical reaction unknown-----		1.04	2.74	7.1	75.8	17.44	792	258	None
Ammonium phosphate, monobasic (NH ₄ H ₂ PO ₄)-----	45.8			2.09	5.73	7.0	69.8	15.75	766	229	None
				3.24	9.05	5.8	65.8	14.57	754	198	None
				5.40	15.42	6.6	22.9	6.72	220	89	None
				7.60	20.58	7.5	18.4	4.60	190	73	None
Zinc chloride (ZnCl ₂)-----	47.8	Zinc ammonium phosphate (ZnNH ₄ PO ₄)-----	62.4	1.19	3.27	7.0	72.6	17.58	773	248	None
Ammonium phosphate, monobasic (NH ₄ H ₂ PO ₄)-----	40.3	Ammonium chloride (NH ₄ Cl)-----	37.6	2.27	6.01	6.4	67.9	14.77	760	204	None
Ammonia gas (NH ₃)-----	11.9			3.74	10.54	5.7	37.8	6.69	492	132	None
				6.15	17.22	6.0	18.1	4.52	183	83	None
				8.55	22.92	5.9	16.3	4.08	176	64	None

¹ Calculated on the basis of air-dry wood.² Based on the weight of the treated wood after drying at 215° to 220° F. for 24 hours.³ When the flaming stopped.⁴ Calculated by dividing the loss in weight when flaming stopped by the time of flaming.⁵ Calculated by dividing the maximum temperature by the length of time of its occurrence.⁶ Based on untreated wood as "moderate".

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solution and of ammonia gas required to complete the chemical reaction are shown in Table 3. With the treatments that did not include ammonia gas the extent to which the chemical reaction is completed is not known, hence the proportions of compound present in the wood are not given. With the treatments in which ammonia gas was used, the proportions of compounds formed can be calculated with some degree of certainty and hence are shown in the table.

The records of absorptions, moisture content of the treated wood when tested, and data on fire resistance are also given in Table 3. In Figures 3 and 4 the loss in weight during flaming and the maximum temperature are plotted against absorptions and the curve for diammonium phosphate is shown for comparison. The four treatments rate in effectiveness in the following order from the most to the least effective:

1. Magnesium chloride, monoammonium phosphate, and ammonia gas.
2. Magnesium chloride, monosodium phosphate, and ammonia gas.
3. Magnesium chloride and monoammonium phosphate.
4. Magnesium chloride and monosodium phosphate.

The ammonia-gas treatment added considerable effectiveness to both combinations of salts. In both treatments with ammonia gas the proportion of magnesium ammonium phosphate to other compounds present in the wood was closely the same. The kind and amounts of by-products, namely, ammonium chloride and sodium chloride, formed were also factors in determining the effectiveness of the treatment. Since ammonium chloride is more fire retardant than sodium chloride the treatments in which ammonium chloride was formed as a by-product would logically be expected to be more effective than those in which sodium chloride was formed.

The magnesium chloride-monoammonium phosphate-ammonia gas treatment, the most effective of the group, appears to possess one or two advantages over a straight ammonium phosphate treatment. More than half of the chemical in the wood is highly insoluble and therefore should be more permanent under service conditions favoring leaching. It is also possible that the combination of chemicals would be cheaper than either monoammonium or diammonium phosphate alone.

Zinc Phosphate Treatments

The zinc chloride and monoammonium phosphate (with and without ammonia-gas treatment) combinations appeared in the extensive survey to warrant more careful study. Two series of absorptions were therefore made and tested, one with ammonia-gas treatment and the other without. The zinc chloride and monoammonium phosphate were again used in amounts proportional to their molecular weights. The proportions of the chemicals used and of those theoretically formed in the wood, absorptions, and other test data are also shown in Table 3.

The losses in weight during flaming and maximum temperatures obtained are plotted in Figure 5 against absorptions. Compared with diammonium phosphate the combination of zinc chloride and monoammonium phosphate was nearly as effective as in the heavy absorptions. In the lighter absorptions the combination was distinctly less effective. Treatment with ammonia gas did not increase the effectiveness as much as in the magnesium phosphate treatments.

According to the literature zinc ammonium phosphate is still more insoluble and thus less subject to leaching than magnesium ammonium phosphate. It also represents a somewhat larger proportion of the total chemical in the wood than is true of magnesium phosphate treatments. Consequently, more of the fire-retardant effectiveness of the zinc ammonium phosphate treatment should be relatively permanent under conditions that favor leaching.

The zinc ammonium phosphate treatment (with ammonia gas) should not be expected to give protection against decay, since the zinc compound is not sufficiently soluble in water to give a toxic concentration. The zinc chloride and monoammonium phosphate (without ammonia gas) combination, however, would give protection against decay, since the zinc, combined with either radical (chloride or monobasic phosphate), is sufficiently soluble to be toxic to wood-destroying fungi. Furthermore, the two chemicals used in the treatment may be combined in all proportions and still obtain a clear treating solution, thus permitting the selection of a mixture that will give more or less protection against fire and decay, respectively, as desired. The principal disadvantage of the treatment would be the tendency of the compounds to leach under damp conditions, since both chemicals are readily soluble.

Other Promising Methods of Producing the Insoluble Phosphates

The combinations of chemicals used in the magnesium phosphate and zinc phosphate treatments may not give the lowest cost nor the greatest fire-retardant effect. In fact, since the starting of intensive tests on these compounds extensive tests have been made with the oxides of magnesium and zinc, each in combination with phosphoric acid (No. 6 and 9, Table 2.) The results indicate that a greater fire-retardant effect and lower costs are obtained per pound of chemical used than when the chlorides of magnesium or zinc are combined with monoammonium phosphate. The use of the oxides of the metals with acids has the further advantage of avoiding the formation of chlorides, which might be objectionable in use. With the zinc phosphate-ammonium hydroxide treatment (No. 10, Table 2) the use of the oxide of zinc and phosphoric acid will theoretically yield only the highly insoluble zinc ammonium phosphate in the wood. These lines of investigation will be followed further.

When the tests involving oxides were made it was assumed⁴ that, in the solution strength necessary to give an absorption of 5 pounds of chemical per cubic foot of wood, the ratio of phosphoric acid to magnesium oxide must be sufficient to form monobasic magnesium phosphate. Subsequent tests indicated that a clear solution could be obtained when a considerably larger proportion of magnesium oxide was used, a procedure that results in the formation of more magnesium ammonium phosphate in proportion to diammonium phosphate upon treatment with ammonia. Actually the proportions of chemicals required theoretically by the balanced equations need not be strictly adhered to in practice. A treating solution containing either the zinc or the magnesium radical in the presence of either the phosphate or the arsenate radical must be sufficiently acidic to prevent the precipitation of the dibasic phosphate or arsenate of the metal, but aside from this limitation the proportions of the various components may be varied at will. In most of the treatments described in this paper the proportions of chemicals chosen were those that would give the smallest number of products and at the same time the highest possible ratio of insoluble to soluble, thus facilitating the evaluation of the insoluble compounds as fire retardants. It is recognized that these proportions are not necessarily the ideal ones from the standpoint of cost and practical value.

Magnesium Arsenate Treatment

In the extensive survey a combination of trisodium arsenate, arsenic acid, and magnesium chloride, with and without ammonia gas, was used (treatment No. 11, Table 2). The chemical reaction, when ammonia gas is used, would theoretically form magnesium ammonium arsenate ($MgNH_4AsO_4$), ammonium arsenate, and sodium chloride. These compounds were satisfactory in stopping flaming though they had less effect on glowing. The magnesium ammonium arsenate, comprising about 50 percent of the compounds formed in the wood, is quite insoluble. It is inherently extremely toxic, and a saturated solution, although it contains only a small amount of the chemical, is toxic to the wood-destroying fungus Fomes annosus. It is therefore one of those rare compounds that are quite insoluble but at the same time toxic.

Considering its unusual combination of fire resistance, low solubility, and toxicity to fungi, the magnesium ammonium arsenate treatment justifies more intensive investigation.

⁴Solubilities of inorganic and organic compounds. Atherton Seidell. Second edition, page 395.

Gluing Tests on Fire-Resistant Wood

Laboratory tests have been made on the gluing properties of wood treated with six different chemicals, ammonium chloride, ammonium sulphate, diammonium phosphate, monoammonium phosphate, zinc chloride, and a mixture of about 40 percent borax and 60 percent boric acid. Birch lumber 1 inch in nominal thickness, selected for density and freedom from defects, was cut into pieces, 12 inches in length, which were carefully matched so that wood of similar quality was used in all treatments and as untreated controls. The pieces were then treated with concentrations of solutions that gave absorptions of dry chemicals from 3.4 pounds per cubic foot of wood for diammonium phosphate to 5.6 pounds for ammonium sulphate; these absorptions had been found sufficient in the fire-tube to keep the loss in weight of specimens down to about 25 percent. The wood was dried and conditioned slowly after treatment under circumstances that bring untreated wood to 6 or 7 percent moisture content. The treated pieces were then surfaced, glued, reconditioned, cut into test specimens, and the joints tested in shear. The gluing was done with animal, casein, and vegetable (starch) glues, under a range of gluing conditions normal in good factory operations and known from laboratory test to give good joints on untreated wood.

The extent to which the various fire-retardant chemicals affected the gluing of the treated wood varied with the different glues. The most interference occurred with casein glues. All the ammonia salts and the zinc chloride (in the heavy concentrations used) reduced the joint strengths to a considerable extent, especially with a casein glue of low alkalinity. With animal and vegetable glues the interference of the fire-retardant chemicals was less obvious. Ammonium chloride, however, showed some interference with the making of good animal glue joints and ammonium sulphate and monoammonium phosphate interfered somewhat with vegetable glue joints when considerable time elapsed between spreading the glue and pressing. No pronounced interference from the borax and boric-acid mixture could be found with any of the glues, though there was apparently slight interference with casein and vegetable glues. The effects described were found on newly made joints and consequently do not indicate the effect of the chemicals on the permanence or durability of the joints over a long period of time.

Further Work

The work on combinations of chemicals has developed a number of promising leads, which future investigations should follow up. In addition to the combinations specifically described in this report, others of equal promise can be suggested. Some of the treatments worked with in the extensive survey should have more careful study; particular attention should be given to treatments of low cost that give to the wood a combination of desirable properties, such as resistance to fire and to decay. Finally, it will be necessary to study carefully the various properties of the treated wood that are important from a use standpoint.

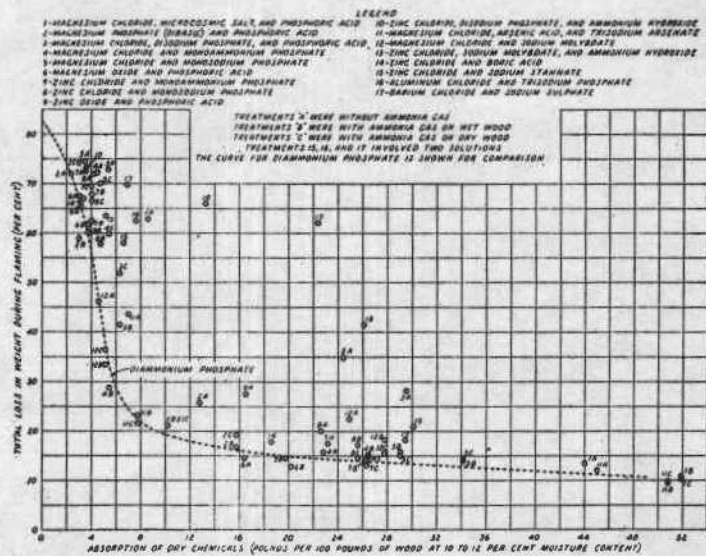


Figure 1.—Loss in weight in fire-tube tests plotted against absorptions for the treatments shown in Table 2.

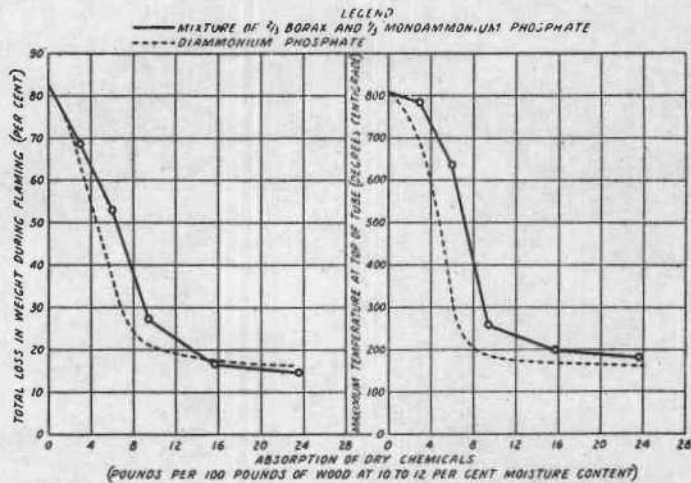


Figure 2.—Fire resistance of borax-monoammonium phosphate mixture compared with diammonium phosphate in intensive survey.

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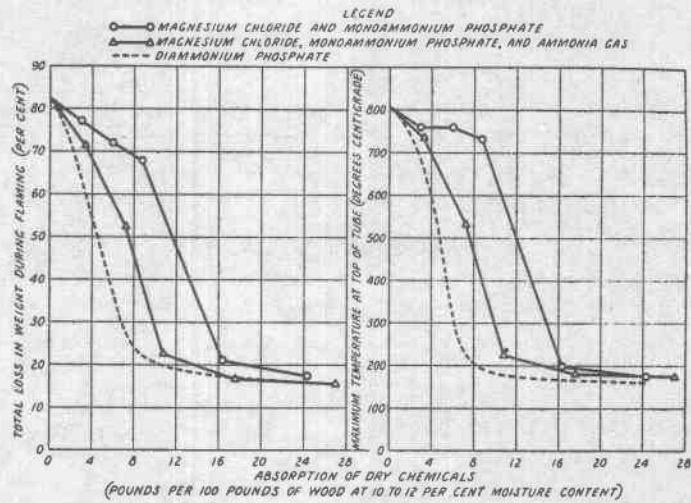


Figure 3.—Fire resistance of magnesium chloride-monoammonium phosphate mixtures compared with diammonium phosphate in intensive survey.

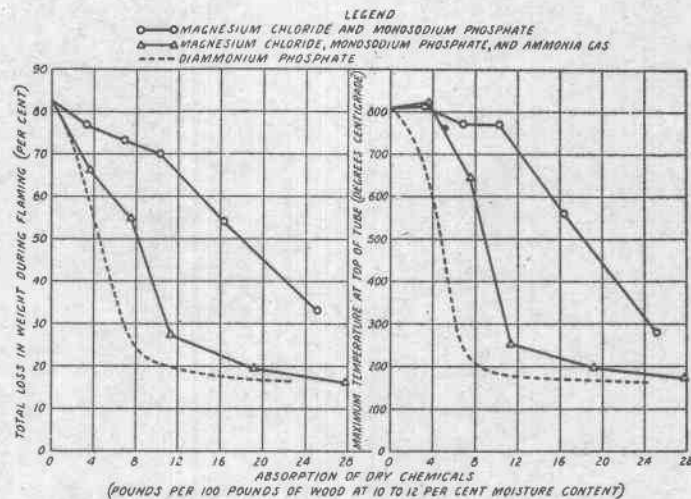


Figure 4.—Fire resistance of magnesium chloride-monosodium phosphate mixtures compared with diammonium phosphate in intensive survey.

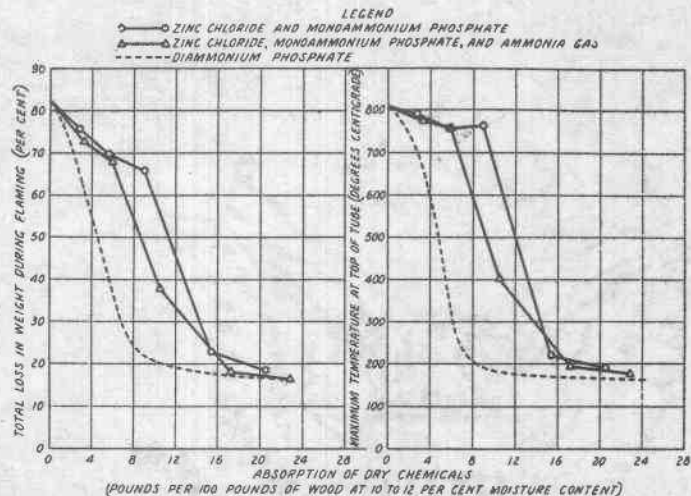


Figure 5.—Fire resistance of zinc chloride-monoammonium phosphate mixtures compared with diammonium phosphate in intensive survey.

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