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Monoammonium Phosphate: Effect on Flammability of Excelsior and Pine Needles

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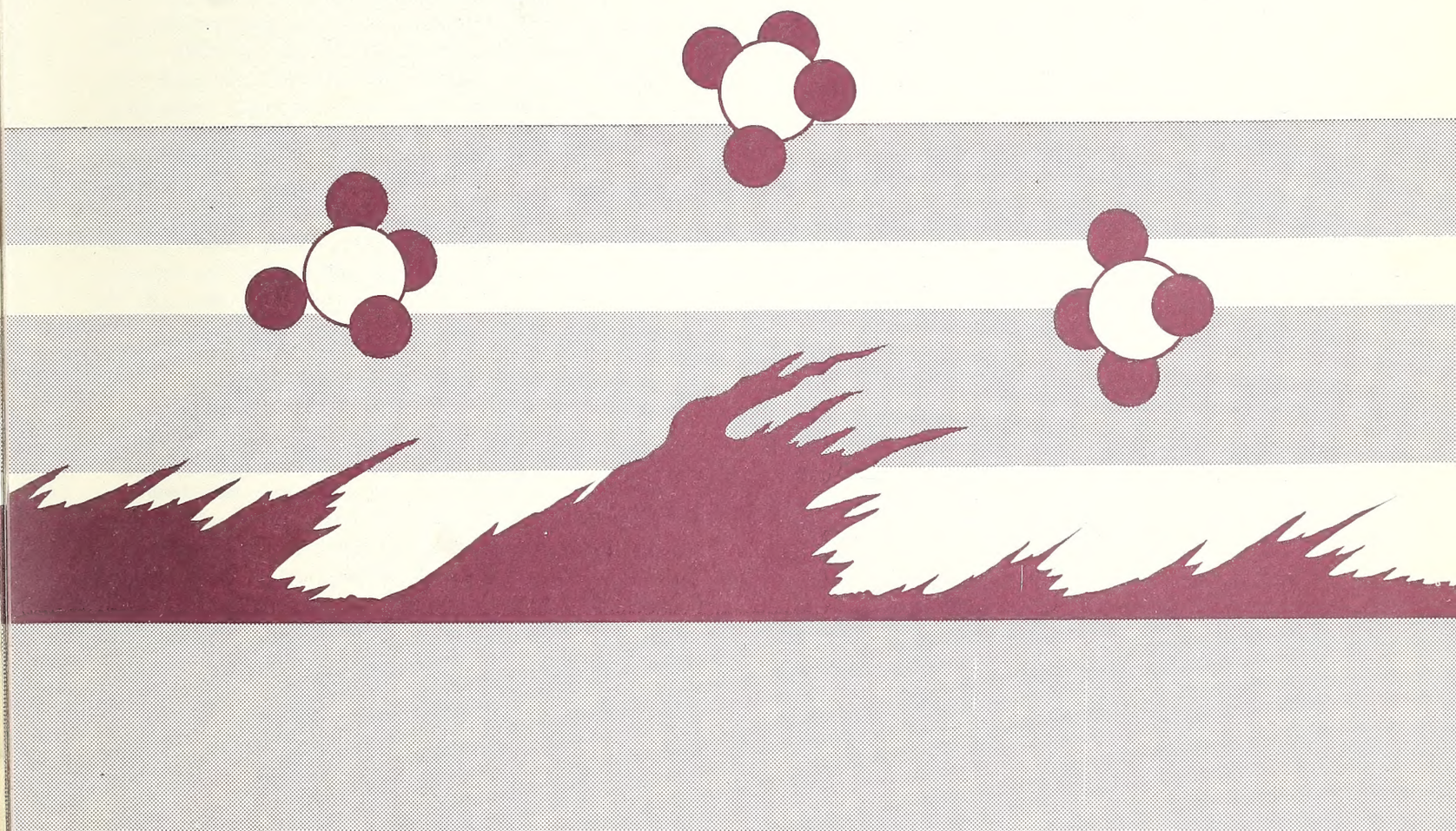

RESEARCH SUMMARY

Treated ponderosa pine needle and aspen excelsior fuel beds were burned to quantify the fire-retarding capabilities of five samples of monoammonium phosphates. The samples were the same except for their manufacturing processes, which could cause chemical impurities that may decrease combustion-retarding effectiveness. Treatment levels were normalized by converting to phosphate equivalents when comparing effectiveness. To obtain about equal penetration, approximately 0.26 gal (1 liter) of a solution containing one of the chemicals was applied to each bed. Different chemical treatment levels were obtained by varying the solution concentrations. Solutions were sprayed onto the fuel beds from a fan-type nozzle, and after drying completely, the fuel was burned in a 5-mi/h (8-km/h) wind at 90° F (32.2° C) and 20 percent relative humidity. Analysis of covariance and percent reduction in combustion rates were methods used to compare levels of effectiveness. Test results indicate no significant differences between the combustion-retarding abilities of the five monoammonium phosphates, and all proved to be as effective as standard diammonium phosphate when compared at equivalent phosphorous application levels.

THE AUTHOR

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INTRODUCTION

Forest fire retardants were first operationally delivered by aircraft in the mid-1950's, and consisted mainly of chemicals that retained water and amassed thick layers on aerial fuels. The first chemical to be used extensively was sodium-calcium borate (commonly called "borate") that not only thickened the water, but had some fire-retarding properties when dry (Miller and Wilson 1957). Borate was toxic to plants, erosive on pumps, and costly because of the required mix ratio. Bentonite clay was introduced to overcome some of the problems caused by borate, but it only thickened the water and had no long-term retarding properties when dry (Phillips and Miller 1959). Borate and bentonite use was phased out when chemicals (called long-term retardants) were introduced that more effectively retard combustion, even when completely dry.

Experiments with long-term chemicals were performed by Truax (1939) to quantify the fire-retarding abilities of water solutions of several commonly used chemicals and chemical combinations, and to determine the feasibility of using them on wildfires. These were some of the same chemicals that had been used successfully for impregnating and fireproofing building materials since the early 1900's. Studies by Truax and later by Tyner (1941) showed that diammonium and monoammonium phosphate water solutions were the most effective for retarding combustion. Other phosphate compounds have been tested, but the ammonium phosphates are the most chemically available for affecting pyrolysis. George and others (1977) reflect that phosphate compounds formed with Fe, Ca, or Mg usually are ineffective because of their high temperature requirements for decompositions and thus their unavailability in terms of altering pyrolysis and combustion reactions. Operation Firestop (1955a, 1955b) tested some phosphate chemicals along with borate, but because of the test methods and interpretation of results, borate was considered the superior fire-retarding chemical, and thus its use as the original aerial-delivery fire retardant.

Monoammonium phosphate (MAP) was dropped from a TBM airtanker onto forest fires in Georgia (Johansen 1959) with good results. Soon after, attempts were made to thicken the MAP with clays or gums (Johansen and Shimmel 1963) for better adherence to aerial fuels. Use of MAP was abandoned when Pyro, a liquid mixture of ammonium phosphate species, was introduced in the Southeast (Johansen and Crow 1965). Pyro was comparatively inexpensive and required only dilution with water and pumping into the airtanker. MAP was considered unhandy because it required breaking bags open and mixing with water under agitation. Later developments of mixing equipment resolved most of the limiting mixing procedures.

In 1961 tests were performed (Hardy and others 1962) to compare the effectiveness of several different retardant formulations that were being suggested and introduced by firefighters and chemical companies. Among those chemicals were borate, algin-gel, diammonium phosphate (DAP) thickened with algin and pectin, and ammonium sulfate thickened with attapulgite clay. The tests showed that the sulfate- and phosphate-based materials were superior to borate and water thickeners, especially after all the water had evaporated. Fire-Trol® (formulated with ammonium sulfate and clay thickener) and Phos-Chek® (formulated with diammonium phosphate and gum thickener) brand fire retardants were first produced commercially about 1962, and formulations containing various dry chemical combinations have since been the principal fire retardants used in the United States for combating wildfires. Several studies have been conducted to better quantify the combustion-retarding effectiveness of sulfates and phosphates, and to identify their basic fire-retarding mechanisms (George and Susott 1971; George and Blakely 1972; Browne and Tang 1963; and Eickner 1962). Other phosphate-based retardants have since been used extensively: Pyro, previously mentioned, and Fire-Trol 931, made of 10-34-0 ammonium polyphosphate (Wood 1970; George 1971; George and others 1977).

In recent years, many of the chemicals used to prepare retardant formulations—basic retardant chemicals as well as additives for coloring and corrosion inhibition—have increased severalfold in price and, in some cases, have become difficult or impossible to obtain. For example, for several years the DAP used in retardants was produced as a byproduct from the conversion of coal to coke. Phosphoric acid (H_3PO_4) was used to remove (scrub) ammonia bearing-off gases from manufacturing effluents. In this reaction, either mono- or diammonium phosphate is produced, but unfortunately, the cost of using these products has become prohibitive. MAP and DAP are also manufactured by bubbling ammonia gas through H_3PO_4. Much of the high cost of combining ammonia and acid is in the costs of ammonia or nitrogen (N); therefore, it is more economical to add only one ammonia (NH_3) to each phosphate (PO_4) to make $NH_4H_2PO_4$(MAP). In other cases, retardant users are searching for chemicals that are less expensive because of their formulas and/or manufacturing processes, but which are still cost-effective.

This study quantified the fire-retarding effectiveness of monoammonium phosphate chemicals from different sources and compared their effectiveness to diammonium phosphate (the basic fire retardant chemical in some currently approved retardants). Tests were performed with five MAP samples manufactured by various companies and/or processes.

The samples were basically the same except for minor differences in composition and manufacturing process. The chemicals and their apparent differences are:

- M-MAP – Fisher Scientific, ACS grade, granular form. Contains less than 0.03 percent impurities.
- S-MAP – Technical grade, granular form. Produced from technical grade phosphoric acid (white acid process) that has been neutralized with anhydrous ammonia.
- D-MAP – Technical grade, crystalline form. Technical grade phosphoric acid neutralized by ammonia-rich gases that are given off by burning coal to make coke.
- T-MAP – Technical grade, crystalline form. Produced from technical grade phosphoric acid that has been neutralized with anhydrous ammonia. (T-MAP and S-MAP are manufactured by similar processes, but by different companies.)
- A-MAP – Technical grade, crystalline form. Manufactured from wet-process phosphoric acid and then repurified to produce a technical grade product with less than 0.1 percent of impurities.

The phosphate quantities were calculated as P_2O_5 equivalents to aid effectiveness comparisons because all MAP or DAP formulations should be equally effective if the phosphate (P_2O_5) in each (the principal fire-retarding element) is present and available in equal concentrations.

The study was an indirect way to determine if the manufacturing process, manufacturer, or quality of fire retardant chemical causes any reduced availability of the phosphorus at the precise time or temperature during pyrolysis when the retardant would have the needed effect (George and Susott 1971). Comparison of like quantities of different chemicals that are equally effective fire retardants will indicate how much added chemical is necessary to increase the total available phosphorus in a particular chemical formula. All effectiveness data are compared to DAP because it has been used as a standard of comparison since 1970 (George and Blakely 1972).

STUDY METHODS

Fuel Beds

Combustion-retarding effectiveness data were gathered by burning mat-type fuel beds treated with different retardant chemicals. Two fuels were used for the study—ponderosa pine needles and aspen excelsior. The pine needles, gathered locally, were cleaned of debris, grass, and sticks, and stored to dry. The excelsior was ordered in compact bales that were pulled apart and allowed to come to equilibrium moisture content under inside conditions. The two fuels were used to determine the fire-retarding effectiveness of chemicals on fuels with a high cellulose (42 percent) and a low crude fat (1 percent) content (excelsior), and fuels with a low cellulose (18 percent) and a high crude fat (10 percent) content (needles). These fuels were not necessarily used to duplicate natural wildfire conditions, but because they (1) are relatively easy to obtain, (2) respond to temperature and humidity changes, (3) are similar in chemical content to many fuels encountered on wildland fires, and (4) provide predictably reproducible fires under controlled environmental and fuel moisture conditions.

Standard techniques were used (George and Blakely 1972) for constructing and treating the 8-ft- (2.44-m-) long, 3-inch-(7.62-cm-) deep, 18-inch- (45.72-cm-) wide fuel beds. Each pine needle bed contained 6 lb (2.72 kg) of fuel, and each excelsior bed contained 4 lb (1.81 kg) of fuel. The fuel moisture content (measured by xylene distillation) was between 4 and 5.5 percent for excelsior, and 6 and 7.5 percent for needles after preconditioning and before chemical treatment application.

Adjustments for Differences in Untreated Fuel Burning Rates

The burning characteristics of different batches of untreated fuels have varied somewhat in previous laboratory studies. Pine needles gathered in the fall have combustion rates that differ from those gathered in the spring, and fall needles may vary slightly from year to year. The same is true of batches of commercially prepared excelsior that may vary somewhat in untreated flame spread rates and total weight-loss rate. Because of the variations in untreated fuels used in this study, adjustments were necessary to make burning data comparable. One method was to calculate the percentage that untreated fuel combustion rates for individual fires are reduced by each treatment. By this means, the differences in untreated burning rates (flame spread and fuel bed weight loss) are taken into account and numerical comparisons can be made. A 0 rating indicates that a retardant has no effect on combustion, and a 100 rating indicates that a chemical totally stops flaming and glowing combustion. The percentage rating is calculated using the flame-spread rate and weight-loss rate for untreated and treated fuels (pine needles and aspen excelsior). For comparisons to be valid, treatment levels for different fires or chemicals must be approximately equal. Spread- and weight-loss rates for treated fuels are calculated as percentages of spread- and weight-loss rates for untreated fuels (percent reduction). Equal numbers of fires for each treatment level (or weighted averages) must be used if statistically meaningful percent reduction factors are to be averaged for two or more treatment levels.

Another method was to adjust each treated fuel burning rate by a percentage corresponding to the differences in average untreated burning rates for different batches of fuel. Recently used untreated fuels have burning rates varying from 5 to 17 percent higher than rates for untreated fuels used in the past when the DAP and M-MAP burns were conducted; therefore, in this study S-MAP burning rates have been adjusted downward. This adjustment also permits the use of the actual spread and weight-loss rates for computations and graphing, rather than conversion to percent reduction of untreated rates. Table 1 shows the untreated averages and the differences between needles and excelsior used in 1970 and 1980.

Table 1.—Factors for adjusting treated bed burning rates for differences in untreated burning rates

Year	Pine needles						Aspen excelsior					
	Average R/S[1]	Std. dev.	N	Average R/W[2]	Std. dev.	N	Average R/S	Std. dev.	N	Average R/W	Std. dev.	N
	Ft/min			*g/min*			*Ft/min*			*g/min*		
1980	2.03	0.10	4	345	3.0	4	4.26	0.10	4	529	35.1	4
1970	1.81	.03	12	294	3.3	11	4.04	.14	9	459	6.1	9
Difference	0.22			51			0.22			70		
	$1 - \frac{0.22}{2.03} = 0.892$			$1 - \frac{51}{345} = 0.852$			$1 - \frac{0.22}{4.26} = 0.948$			$1 - \frac{70}{529} = 0.868$		
Adjustment	0.892			0.852			0.948			0.868		

[1]R/S = flame spread rate.
[2]R/W = burning fuel rate of weight loss.

Chemical Application

A pressurized sprayer with a fan-shaped spray pattern was used to apply retardant (George and Blakely 1972). The sprayer was calibrated for each different retardant chemical and concentration to produce a spray pattern that would coat the fuels uniformly. The volume of chemical solution applied to each bed was held as closely as practical to 0.26 gal (1 liter), and the different levels of the dried chemical applied to different beds were varied by adjusting the solution concentrations. After treatment, fuel beds were dried under environmental conditions of 90° F ± 2° (32.2° C ± 2°), and 20 percent relative humidity ± 2 percent, until all the solution water had been evaporated and the fuel moisture content was about the same as before treatment. Low-velocity fans were used to keep air moving above the treated beds so drying would occur uniformly throughout the depth of the bed. After all the water had evaporated (determined by frequent weighing on an electronic balance), beds were burned in a wind tunnel under conditions of 90° F (32.2°), 20 percent relative humidity, and in a 5-mi/h (8-km/h) wind. (These environmental conditions can be related to wildfire situations by the following: When needles and excelsior are classed as fuel type U, the National Fire-Danger Rating System [NFDRS] grades fires in untreated fuels as spread component 5, energy release rate 38, and burning index 34.)

Burning Procedures

A 3-ft- (0.91-m-) long untreated fuel bed of the same fuel type and loading as that in the treated bed was ignited and allowed to burn into the treated fuel. As the fuel burned, the rate of weight loss was continuously measured by four load cells mounted beneath the bed (George and Blakely 1970), and data were recorded on a Tektronix® 4051 microcomputer. The flame spread was monitored visually, and an event marker was used to record the flame front progress. After each fire, the recorded data were entered into a computer program, and flame spread rate and total fuel bed weight loss rate were calculated and plotted. These two parameters were used for comparing the effectiveness of different chemicals and treatment levels.

RESULTS

About 250 treated and untreated beds were burned. Results of burning pine needles and aspen excelsior treated with DAP have been reported previously (George and Blakely 1972), and are used as a standard for USDA Fire Retardant Qualification Tests. The M-MAP-treated beds were burned during the same period as DAP-treated beds (George and Blakely 1972), and therefore untreated ponderosa pine and aspen excelsior from the same untreated fuel batches were used. (The M-MAP data have not been published previously.) The remaining fires were conducted using untreated fuels collected several years later. Adjustments were made (table 1) in the data for recent burns to compensate for differences in untreated burning rates. Tables for all MAP-treated (except M-MAP) beds contain columns of adjusted spread- and weight-loss rates that were used for regression analysis. These data and those for DAP and M-MAP are shown in tables 2 through 9.

Table 2.—Summary of test data for DAP-treated aspen excelsior fuel beds (from George and Blakely 1972)

Treatment solutiom				Anhydrous chemical		Rate of flame spread R/S	Rate of weight loss R/W
Chemical by weight	Solution density	Solution quantity		DAP	P_2O_5		
Percent	*g/cm³*	*g*	*ml*	---- *g/ft²* ----		*Ft/min*	*g/min*
2.5	1.014	1000	986	2.08	1.12	3.01	200
2.5	1.014	990	976	2.06	1.11	2.96	320
2.5	1.014	970	957	2.02	1.09	3.12	225
2.5	1.014	985	971	2.05	1.10	2.82	296
5.0	1.029	1030	1001	4.29	2.31	1.51	188
5.0	1.029	950	923	3.96	2.13	1.33	213
5.0	1.029	990	962	4.12	2.22	1.01	126
5.0	1.029	936	910	3.90	2.10	1.27	143
5.0	1.029	917	891	3.82	2.06	1.16	170
7.5	1.042	1000	960	6.25	3.36	.61	114
7.5	1.042	980	940	6.13	3.30	.70	114
7.5	1.042	970	931	6.06	3.26	.72	133
7.5	1.042	1025	984	6.40	3.44	.39	51
10.0	1.056	1000	947	8.33	4.48	.61	71
10.0	1.056	995	942	8.29	4.46	.53	102
10.0	1.056	1040	985	8.67	4.66	.61	79
12.5	1.072	1030	961	10.73	5.77	.35	56
12.5	1.072	1010	942	10.52	5.66	.46	92
12.5	1.072	1005	938	10.47	5.63	.41	59

Table 3.—Summary of test data for DAP-treated ponderosa pine needle fuel beds (from George and Blakely 1972)

Treatment solutiom				Anhydrous chemical		Rate of flame spread R/S	Rate of weight loss R/W
Chemical by weight	Solution density	Solution quantity		DAP	P_2O_5		
Percent	*g/cm³*	*g*	*ml*	---- *g/ft²* ----		*Ft/min*	*g/min*
2.5	1.014	975	962	2.03	1.09	1.46	223
2.5	1.014	965	952	2.01	1.13	1.68	233
2.5	1.014	955	942	1.99	1.07	1.55	202
2.5	1.014	1000	986	2.08	1.12	1.70	196
5.0	1.029	1035	1006	4.31	2.32	1.56	205
5.0	1.029	995	967	4.15	2.23	1.27	160
5.0	1.029	990	962	4.12	2.22	1.08	169
5.0	1.029	1000	972	4.17	2.24	1.26	184
5.0	1.029	980	952	4.08	2.20	1.39	191
7.5	1.042	1000	960	6.25	3.36	1.36	180
7.5	1.042	1010	969	6.31	3.39	1.21	164
7.5	1.042	975	936	6.09	3.28	1.25	200
7.5	1.042	1025	984	6.41	3.45	.93	170
10.0	1.056	1020	966	8.50	4.57	.82	163
10.0	1.056	995	942	8.29	4.46	.69	174
10.0	1.056	1055	999	8.79	4.73	.75	161
10.0	1.056	1010	956	8.42	4.53	.94	196
12.5	1.072	1010	942	10.52	5.66	.69	131
12.5	1.072	965	900	10.05	5.41	.70	147
12.5	1.072	1050	979	10.94	5.89	.43	111
15.0	1.084	1025	946	12.81	6.89	.28	77
15.0	1.084	960	886	12.00	6.46	.68	137
15.0	1.084	1000	923	12.50	6.73	.50	129
15.0	1.084	990	913	12.38	6.66	.35	101
17.5	1.108	1050	948	15.31	8.24	.26	71
17.5	1.108	980	884	14.29	7.69	.37	94
17.5	1.108	1015	916	14.80	7.96	.39	97
17.5	1.108	1025	925	14.94	8.04	.38	79
20.0	1.111	1005	904	16.75	9.01	.33	76
20.0	1.111	1038	934	17.30	9.31	.24	63
20.0	1.111	1081	973	18.02	9.69	.29	--

Table 4.—Summary of test data for M-MAP-treated aspen excelsior fuel beds

Treatment solutiom				Anhydrous chemical		Rate of flame spread R/S	Rate of weight loss R/W
Chemical by weight	Solution density	Solution quantity		MAP	P_2O_5		
Percent	*g/cm³*	*g*	*ml*	---- *g/ft²* ----		*Ft/min*	*g/min*
2.5	1.014	1010	996	2.10	1.30	2.48	297
2.5	1.014	1010	996	2.10	1.30	2.63	294
2.5	1.014	995	981	2.07	1.28	2.23	264
5.0	1.029	1005	977	4.19	2.59	.57	113
5.0	1.029	1135	1103	4.73	2.92	.52	118
5.0	1.029	1055	1025	4.40	2.72	1.06	133
7.5	1.042	1030	988	6.44	3.98	.60	103
7.5	1.042	1100	1056	6.88	4.25	.68	79
7.5	1.042	1000	960	6.25	3.86	.73	120
10.0	1.056	930	881	7.75	4.78	.74	117
10.0	1.056	960	909	8.00	4.94	.43	82
10.0	1.056	965	914	8.04	4.96	.40	83

Table 5.—Summary of test data for M-MAP-treated ponderosa pine needle fuel beds

Treatment solutiom				Anhydrous chemical		Rate of flame spread R/S	Rate of weight loss R/W
Chemical by weight	Solution density	Solution quantity		MAP	P_2O_5		
Percent	*g/cm³*	*g*	*ml*	----- *g/ft²* -----		*Ft/min*	*g/min*
2.5	1.014	990	976	2.06	1.27	1.56	--
2.5	1.014	1035	1021	2.15	1.33	1.26	202
2.5	1.014	1040	1026	2.16	1.33	1.61	146
5.0	1.029	1035	1006	4.31	2.66	1.12	258
5.0	1.029	1090	1059	4.54	2.80	1.83	206
5.0	1.029	1045	1016	4.35	2.69	1.34	186
7.5	1.042	1070	1027	6.69	4.13	.74	94
7.5	1.042	1060	1017	6.63	4.09	.50	128
7.5	1.042	1070	1027	6.69	4.13	.70	147
10.0	1.056	1100	1042	9.16	5.65	.88	117
10.0	1.056	1135	1075	9.46	5.84	.73	134
10.0	1.056	965	914	8.04	4.96	.83	152
12.5	1.072	925	863	9.63	5.94	.50	87
12.5	1.072	940	877	9.79	6.04	.44	113
12.5	1.072	1040	970	10.83	6.69	.47	94
12.5	1.072	1085	1012	11.30	6.98	.47	91
12.5	1.072	1010	942	10.52	6.49	.43	80
12.5	1.072	1115	1040	11.61	7.17	.42	87
15.0	1.084	1125	1038	14.1	8.70	.45	120
15.0	1.084	1060	978	13.3	8.21	.47	123
17.5	1.108	1135	1024	16.55	10.22	.21	56
17.5	1.108	1115	1006	16.26	10.04	.34	59
17.5	1.108	1080	975	15.75	9.72	.25	54

Table 6.—Summary of test data for S-MAP-treated aspen excelsior fuel beds

Treatment solutiom				Anhydrous chemical		Rate of flame spread[1] R/S		Rate of weight loss[1] R/W	
Chemical by weight	Solution density	Solution quantity		MAP	P_2O_5				
Percent	*g/cm³*	*g*	*ml*	---- *g/ft²* ----		*Ft/min*		*g/min*	
2.5	1.014	992	978	2.06	1.28	2.53	2.40	216	187
2.5	1.014	988	974	2.06	1.27	2.41	2.28	223	194
2.5	1.014	1032	1018	2.15	1.33	1.79	1.70	171	148
5.0	1.028	1032	1004	4.30	2.65	.82	.78	--	--
5.0	1.029	1009	981	4.20	2.60	.70	.66	136	118
5.0	1.028	1041	1013	4.34	2.68	1.27	1.20	247	214
5.0	1.028	1076	1047	4.48	2.77	.98	.93	--	--
5.0	1.029	1022	994	4.26	2.63	.59	.56	134	116
7.5	1.042	1051	1009	6.57	4.05	.91	.86	223	194
7.5	1.042	1009	968	6.31	3.90	.80	.76	124	108
7.5	1.042	1034	992	6.46	3.99	.71	.67	137	136
10.0	1.056	1047	991	8.73	5.39	.46	.44	126	109
10.0	1.056	1061	1005	8.84	5.46	.58	.55	117	102
10.0	1.056	1046	991	8.72	5.38	.58	.55	58	50

[1]Adjusted for difference in untreated fuel burning rate.

Table 7.—Summary of test data for S-MAP-treated ponderosa pine needle fuel beds

Treatment solutiom			Anhydrous chemical		Rate of flame spread[1] R/S		Rate of weight loss[1] R/W	
Chemical by weight	Solution density	Solution quantity	MAP	P_2O_5				
Percent	*g/cm³*	*g*	*ml*	*---- g/ft² ----*		*Ft/min*		*g/min*	
2.5	1.014	1009	995	2.10	1.30	1.78	1.59	244	203
2.5	1.014	985	971	2.05	1.27	1.52	1.36	259	221
2.5	1.014	985	971	2.05	1.27	1.88	1.68	251	214
2.5	1.014	995	981	2.07	1.28	2.25	2.01	212	181
2.5	1.014	1006	992	2.10	1.29	1.91	1.70	244	208
5.0	1.028	1024	996	4.27	2.63	1.40	1.25	200	170
5.0	1.028	1044	1016	4.35	2.69	1.57	1.40	209	178
7.5	1.042	1024	983	6.40	3.95	1.45	1.29	179	156
7.5	1.042	1031	989	6.44	3.98	1.29	1.15	206	176
7.5	1.042	1016	975	6.35	3.92	1.12	1.00	190	162
7.5	1.042	1038	996	6.49	4.00	1.11	.99	138	118
7.5	1.042	1060	1017	6.63	4.09	1.18	1.05	129	110
7.5	1.042	1024	983	6.40	3.95	1.07	.95	162	138
10.0	1.056	1021	967	8.51	5.25	.93	.83	167	142
10.0	1.056	980	928	8.17	5.04	.94	.84	129	110
10.0	1.056	1051	995	8.76	5.41	.86	.77	151	129
12.5	1.071	1032	964	10.75	6.64	.72	.64	159	135
12.5	1.071	1032	964	10.75	6.64	.82	.73	136	116
12.5	1.072	1060	989	11.04	6.82	.59	.53	83	71
12.5	1.072	1062	991	11.06	6.82	.47	.42	102	87
15.0	1.084	1081	997	13.51	8.34	.52	.46	118	101
15.0	1.084	1152	1063	14.40	8.89	.48	.43	108	92
15.0	1.084	1107	1021	13.84	8.54	.41	.37	93	79

[1]Adjusted for differences in untreated fuel burning rates.

Table 8.—Summary of test data for treated aspen excelsior fuel beds

Chemical treatment	Treatment solutiom				Anhydrous chemical		Rate of flame spread[1] R/S		Rate of weight loss[1] R/W	
	Chemical by weight	Solution density	Solution quantity		MAP	P_2O_5				
	Percent	*g/cm³*	*g*	*ml*	*---- g/ft² ----*		*Ft/min*		*g/min*	
T-MAP	5.0	1.029	1046	1017	4.36	2.69	1.01	.96	236	205
	5.0	1.029	1048	1018	4.37	2.70	.94	.89	192	167
	5.0	1.029	1088	1057	4.53	2.80	.83	.79	187	162
	10.0	1.059	1059	1000	8.83	5.45	.39	.37	97	84
	10.0	1.059	1018	961	8.48	5.24	.59	.56	110	95
	10.0	1.059	1010	954	8.42	5.20	.52	.49	108	94
D-MAP	5.0	1.029	1054	1024	4.39	2.71	.89	.84	--	--
	5.0	1.029	1039	1010	4.33	2.67	.91	.86	178	155
	5.0	1.029	1059	1029	4.41	2.72	.60	.57	198	172
	10.0	1.059	1019	962	8.49	5.24	.40	.38	92	80
	10.0	1.059	1024	967	8.53	5.27	.40	.38	84	73
	10.0	1.059	1021	964	8.51	5.25	.54	.51	95	82
A-MAP	5.0	1.029	1028	999	4.28	2.64	.98	.93	156	135
	5.0	1.029	1032	1003	4.30	2.65	.72	.68	144	125
	5.0	1.029	1010	982	4.21	2.60	.49	.46	92	80
	10.0	1.059	1045	987	8.71	5.38	.33	.31	88	76
	10.0	1.059	1049	991	8.74	5.40	.43	.41	134	116
	10.0	1.059	1021	965	8.51	5.25	.54	.51	85	74

[1]Adjusted for differences in untreated fuel burning rates.

Table 9.—Summary of test data for treated ponderosa pine needle fuel beds

Chemical treatment	Treatment solutiom				Anhydrous chemical		Rate of flame spread[1] R/S		Rate of weight loss[1] R/W	
	Chemical by weight	Solution density	Solution quantity		MAP	P_2O_5				
	Percent	*g/cm³*	*g*	*ml*	---- *g/ft²* ----		*Ft/min*		*g/min*	
T-MAP	5.0	1.029	1041	1012	4.34	2.68	1.54	1.37	188	160
	5.0	1.029	1033	1004	4.40	2.66	1.25	1.12	172	147
	5.0	1.029	1034	1005	4.31	2.66	1.33	1.19	204	174
	10.0	1.059	1005	949	8.38	5.17	.82	.73	140	119
	10.0	1.059	1032	975	8.60	5.31	1.09	.97	158	135
	10.0	1.059	1026	967	8.55	5.28	.98	.87	126	107
D-MAP	5.0	1.029	1008	980	4.20	2.59	1.65	1.47	190	162
	5.0	1.029	1050	1021	4.38	2.70	1.46	1.30	199	170
	5.0	1.029	1028	1000	4.28	2.64	1.51	1.35	233	190
	10.0	1.059	1033	976	8.61	5.31	1.13	1.01	--	--
	10.0	1.059	1053	995	8.78	5.42	1.07	.95	160	136
	10.0	1.059	1024	967	8.53	5.27	.84	.75	190	162
A-MAP	5.0	1.029	1037	1008	4.32	2.67	1.67	1.49	169	144
	5.0	1.029	1003	975	4.18	2.58	1.77	1.58	190	162
	5.0	1.029	1040	1011	4.33	2.67	1.41	1.26	202	172
	10.0	1.059	1044	986	8.70	5.37	1.01	.90	181	154
	10.0	1.059	1024	967	8.53	5.27	1.00	.89	168	143
	10.0	1.059	1026	969	8.55	5.28	.93	.83	203	173

[1]Adjusted for differences in untreated fuel burning rates.

In the George and Blakely (1972) study, DAP was tested at several treatment levels, and regression equations were determined for flame spread and weight loss rates on pine needles and aspen excelsior fuels. The same type regression analysis was used with M-MAP and S-MAP, and regressions for all three chemicals have been compared. The analysis was performed to determine if differences exist between the fire-retarding effectiveness of the three source-samples of P_2O_5. To perform statistical tests, it was assumed that there was no significant difference in overall effectiveness when equal levels of P_2O_5 were applied. The hypothesis was tested by covariance analysis and an "F" test.

Rates of flame spread and fuel weight loss (energy release) were fitted by a least-squares method to determine what equation form (quadratic, exponential, logarithmic, reciprocal, and so forth) would fit best and give high correlation coefficients.

Some of the best-fit equations shown in tables 10 and 11 do not have the highest R^2 values possible because data groups that were tested against each other required that their regression equations be of the same form (for example, all ponderosa pine rate-of-spread data are in a second-degree polynomial form so that "F"-tests can be performed). (Equation use is limited to the range included in the data sets and extrapolations beyond the real data cannot be expected to predict accurately.) Three individual and three paired equations were formed with data for each chemical for each test parameter. Then data for all three chemicals (triplet) for each parameter were pooled, and another best-fit equation was formed. Each paired equation was tested against the triplet equations and each individual against each other individual equation by an "F" test method described in figure 1.

Table 10.—Regression equations for flame-spread rate and weight-loss rate for ponderosa pine needles

Treatment	N	Equation	R^2	F^1		Significance[2]
				Variance ratio		*Percent*
Rate of spread						
DAP	31	$Y = 1.9420 - 0.30426X + 0.01313X^2$	0.93			
M-MAP	23	$Y = 1.9419 - 0.31906X + 0.01543X^2$	.81			
S-MAP	24	$Y = 2.0152 - 0.29478X + 0.01255X^2$	.91			
Pooled						
DAP/M-MAP	54	$Y = 1.9523 - 0.31616X + 0.01471X^2$	.88	0.138	(3, 48)	NS
VS All-pooled				.76	(3, 48)	NS
DAP/S-MAP	55	$Y = 1.97073 - 0.29478X + 0.01213X^2$	.91	2.36	(3, 49)	NS
VS/All-pooled				2.64	(3, 49)	NS
M-MAP/S-MAP	47	$Y = 1.99750 - 0.31072X + 0.01410X^2$	.86	1.33	(3, 41)	NS
VS All-pooled				1.55	(3, 41)	NS
DAP/M-MAP/S-MAP	78	$Y = 1.97724 - 0.30872X + 0.01377X^2$	.88			
Rate of weight loss						
DAP	30	$Y = 234.18 - 18.002X$	.87			
M-MAP	22	$Y = 214.02 - 15.693X$	.63			
S-MAP	24	$Y = 217.77 - 16.471X$	.80			
Pooled						
DAP/M-MAP	52	$Y = 227.53 - 17.280X$	.77	.97	(2, 48)	NS
VS All-pooled				1.17	(2, 48)	NS
DAP/S-MAP	54	$Y = 226.56 - 17.261X$	.83	1.94	(2, 50)	NS
VS All-pooled				2.09	(2, 50)	NS
M-MAP/S-MAP	46	$Y = 215.99 - 16.053X$	.72	.11	(2, 42)	NS
VS All-pooled				.57	(2, 42)	NS
DAP/M-MAP/S-MAP	76	$Y = 223.83 - 16.915X$	.78			

[1]Test for the reduction in variance between pooled and unpooled models.
[2]All differences in regressions are not significant below the 99 percent level.

Table 11.—Regression equations for flame-spread rate and weight-loss rate for aspen excelsior

Treatment	N	Equation	R^2	F^1		Significance[2]
				Variance ratio		*Percent*
Rate of spread						
DAP	19	$Y = -0.33231 + 3.5877\ (X^{-1})$	0.97			
M-MAP	12	$Y = -0.27498 + 3.4232\ (X^{-1})$	.92			
S-MAP	14	$Y = -0.05014 + 2.7322\ (X^{-1})$	.87			
Pooled						
DAP/M-MAP	31	$Y = -0.31400 + 3.5369\ (X^{-1})$	.95	0.14	(2, 27)	NS
VS All-pooled				1.12	(2, 27)	
DAP/S-MAP	33	$Y = -0.24474 + 3.3264\ (X^{-1})$	.93	4.19	(2, 29)	95
VS/All-pooled				4.21	(2, 29)	95
M-MAP/S-MAP	26	$Y = -0.16302 + 3.0786\ (X^{-1})$	.89	1.40	(2, 22)	NS
VS All-pooled				2.23	(2, 22)	NS
DAP/M-MAP/S-MAP	45	$Y = -0.25226 + 3.3512\ (X^{-1})$	.93			
Rate of weight loss						
DAP	19	$Y = 264.86 - 121.24\ (\text{Ln } X)$	.81			
M-MAP	12	$Y = 306.48 - 147.31\ (\text{Ln } X)$	.89			
S-MAP	12	$Y = 196.25 - 52.689\ (\text{Ln } X)$	.37			
Pooled						
DAP/M-MAP	31	$Y = 278.43 - 129.26\ (\text{Ln } X)$	.83	1.36	(2, 27)	NS
VS All-pooled				3.20	(2, 27)	NS
DAP/S-MAP	31	$Y = 241.43 - 96.375\ (\text{Ln } X)$	.65	3.74	(2, 27)	95
VS All-pooled				4.38	(2, 27)	95
M-MAP/S-MAP	24	$Y = 249.46 - 97.87\ (\text{Ln } X)$	.61	6.13	(2, 20)	99
VS All-pooled				6.57	(2, 20)	99
DAP/M-MAP/S-MAP	43	$Y = 257.21 - 108.64\ (\text{Ln } X)$	.70			

[1]Test for the reduction in variance between pooled and unpooled models.
[2]All differences in regressions are not significant below the 99 percent level.

Chemical 1,

N_1 points $f_1(x) = a_1 + a_2X + a_3X^2 \ldots a_pX^p$

Chemical 2,

N_2 points $f_2(x) = b_1 + b_2X + b_3X^2 \ldots b_pX^p$

Combine 1 and 2,

$N_1 + N_2$ points $f_3(x) = c_1 + c_2X + c_3X^2 \ldots c_pX^p$

Note: All three regressions must be of the same form; i.e., log, third degree polynomial, and so forth.

$$SS\hat{Y}_1 = \sum_{i=1}^{N_1} (y_1 i - f_1(x_i))^2$$

$$SS\hat{Y}_2 = \sum_{i=1}^{N_2} (y_2 i - f_2(x_i)^2)$$

$$SS\hat{Y} = \sum_{i=1}^{(N_1 + N_2)} (yi - f_3(x_i))^2$$

$SS\hat{Y} - SS\hat{Y}_1 - SS\hat{Y}_2$ = difference in $SS\hat{Y}$

$(N_1 + N_2 - P) - (N_1 - P) - (N_2 - P) = \rho$

$(SS\hat{Y}_1 + SS\hat{Y}_2) / (N_1 + N_2 - P) = MSE(\hat{Y})$

$$F(p, (N_1 + N_2 - 2)) = \frac{\text{Diff } SS\hat{Y}}{\frac{\rho}{MSE(\hat{Y})}}$$

Figure 1.—Method used to calculate F values.

The covariance analysis shows no significant difference between the fire-retarding effectiveness of any of the three chemicals except for one parameter. There appears to be a statistical difference between the regression for M-MAP and S-MAP on excelsior weight loss. The greatest differences are between data at the low treatment levels where small variations in treatment amounts or fuel moisture content will sometimes cause large-scale differences. (The curves show that fire retardant effectiveness is very sensitive to small changes within the low-treatment areas.) Examination of the M-MAP and S-MAP regression data shows that their curves cross at about the 3-g/ft^2 (929-cm^2) treatment level. Apparent differences within each separate regression for each chemical can be caused by variation in fuel chemical composition, environmental conditions, and retardant application. The apparent differences between the fire-retarding abilities of DAP, M-MAP, and S-MAP are because of these variations in testing procedures; and the apparent differences in total effectiveness are therefore not real but because of experimental error. When the three chemicals, two test parameters, and two fuel types are all combined, analysis indicates no real significant differences exist (at the 0.05 level) between the fire- retarding abilities of DAP, M-MAP, and S-MAP.

Two methods were used to evaluate D-MAP, A-MAP, and T-MAP. One method was to plot the individual points on the curves for pooled DAP/M-MAP/S-MAP (P_2O_5 curves) and make general comparisons. The other method was to calculate the flammability reduction percentage for each chemical and compare it to the reduction calculated for the same level of P_2O_5 from the pooled DAP/M-MAP/S-MAP equation. Tables 12 through 14 show the percent reductions for the different chemicals compared to reductions for pooled P_2O_5. The reductions compare closely for all chemicals with none varying more than 0.01 from the pooled P_2O_5 regression.

Table 12.—Reduction of untreated fuel combustion rates caused by D-MAP treatment[1]

		R/S % reduction		R/W	R/W % reduction		Cumulative % reduction	
P_2O_5	R/S	1	2		1	2	1	2
g/ft²	Ft/min			g/min				
				Ponderosa pine				
2.59	1.47	0.19	0.30	162	0.45	0.39		
2.70	1.30	.28	.31	170	.42	.39		
2.64	1.35	.25	.30	190	.35	.39		
5.31	1.01	.44	.60					
5.42	.95	.48	.61	136	.54	.55		
5.27	.75	.59	.60	162	.45	.54		
	Average	0.37	0.45		0.44	0.45	0.41	0.45
				Aspen excelsior				
2.71	0.84	0.79	0.76					
2.67	.86	.79	.75	155	0.66	0.67		
2.72	.57	.86	.76	172	.63	.68		
5.24	.38	.91	.90	80	.83	.83		
5.27	.38	.91	.90	78	.85	.83		
5.25	.51	.87	.90	82	.83	.83		
	Average	0.86	0.83		0.74	0.75	.80	.79
					Total average		0.61	0.62

[1]1 = percent reduction of combustion parameters (flame spread rate and weight loss rate) for untreated fuel bed rates.
2 = percent reducton of combustion parameters that are computed using equivalent treatment amounts and data (flame spread rate or weight loss rate) from pooled data curves for DAP, M-MAP, and S-MAP.

Table 13.—Reduction of untreated fuel combustion rates caused by A-MAP treatment[1]

		R/S % reduction		R/W	R/W % reduction		Cumulative % reduction	
P_2O_5	R/S	1	2		1	2	1	2
g/ft²	Ft/min			g/min				
				Ponderosa pine				
2.67	1.49	0.18	0.31	144	0.51	0.39		
2.58	1.58	.13	.30	162	.45	.39		
2.67	1.26	.30	.31	172	.42	.39		
5.37	901	.50	.60	154	.48	.55		
5.27	.89	.51	.60	143	.51	.54		
5.28	.83	.54	.60	173	.41	.54		
	Average	0.36	0.45		0.46	0.47	0.41	0.46
				Aspen excelsior				
2.64	0.93	0.77	0.75	135	0.71	0.67		
2.65	.68	.83	.74	125	0.73	0.67		
2.60	.46	.89	.74	80	.83	.67		
5.38	.31	.92	.91	76	.84	.84		
5.40	.41	.90	.91	116	.75	.84		
5.25	.51	.87	.90	74	.84	.83		
	Average	0.86	0.83		0.78	0.75	.82	.79
					Total average		0.62	0.63

[1]1 = percent reduction of combustion parameters (flame spread rate and weight loss rate) for untreated fuel bed rates.
2 = percent reducton of combustion parameters that are computed using equivalent treatment amounts and data (flame spread rate or weight loss rate) from pooled data curves for DAP, M-MAP, and S-MAP.

Table 14.—Reduction of untreated fuel combustion rates caused by T-MAP treatment[1]

		R/S % reduction		R/W	R/W % reduction		Cumulative % reduction	
P_2O_5	R/S	1	2		1	2	1	2
g/ft²	Ft/min			g/min				
				Ponderosa pine				
2.68	1.37	0.24	0.31	160	0.46	0.39		
2.66	1.12	.38	.31	147	.50	.39		
2.66	1.19	.34	.31	174	.41	.39		
5.17	73	.60	.59	119	.60	.54		
5.31	.97	.46	.60	135	.54	.54		
5.28	.87	.52	.60	107	.64	.54		
	Average	0.42	0.45		0.53	0.47	0.48	0.46
				Aspen excelsior				
2.69	0.96	0.76	0.75	205	0.55	0.67		
2.70	.89	.78	.75	167	0.64	0.68		
2.80	.79	.80	.77	162	.65	.68		
5.45	.37	.91	.91	84	.82	.84		
5.24	.56	.86	.90	95	.79	.83		
5.20	.49	.88	.90	94	.80	.83		
	Average	0.83	0.83		0.71	0.75	.77	.79
					Total average		0.63	0.63

[1]1 = percent reduction of combustion parameters (flame spread rate and weight loss rate) for untreated fuel bed rates.
2 = percent reducton of combustion parameters that are computed using equivalent treatment amounts and data (flame spread rate or weight loss rate) from pooled data curves for DAP, M-MAP, and S-MAP.

Tables 10 and 11 show the results of regression analysis and "F" tests for regression differences. The program for calculating "F" values is given in figure 1. Figure 2 shows all the weight-loss data on excelsior for DAP, M-MAP, and S-MAP, and the pooled equation is plotted. Figure 3 shows data and the equation for spread rate data on excelsior for DAP, M-MAP, and S-MAP. Figures 4 and 5 are weight-loss and spread-rate data on pine needles for all three chemicals. Figures 6 through 9 show all data points for all three chemicals, and individual best-fit equations are plotted for each chemical.

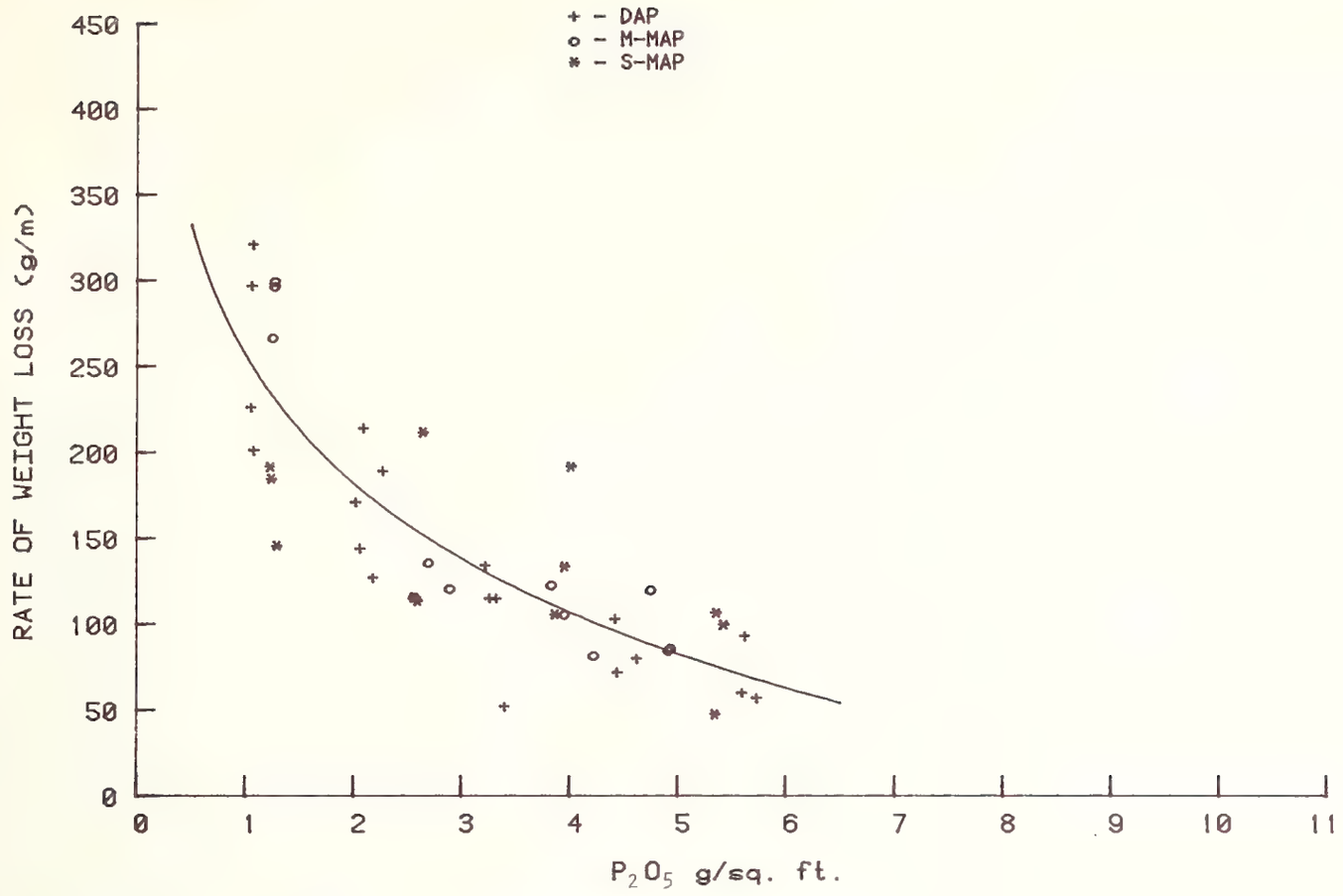

Figure 2.—Effect of DAP, M-MAP, and S-MAP on weight loss rate of excelsior. (Equation for pooled data is plotted.)

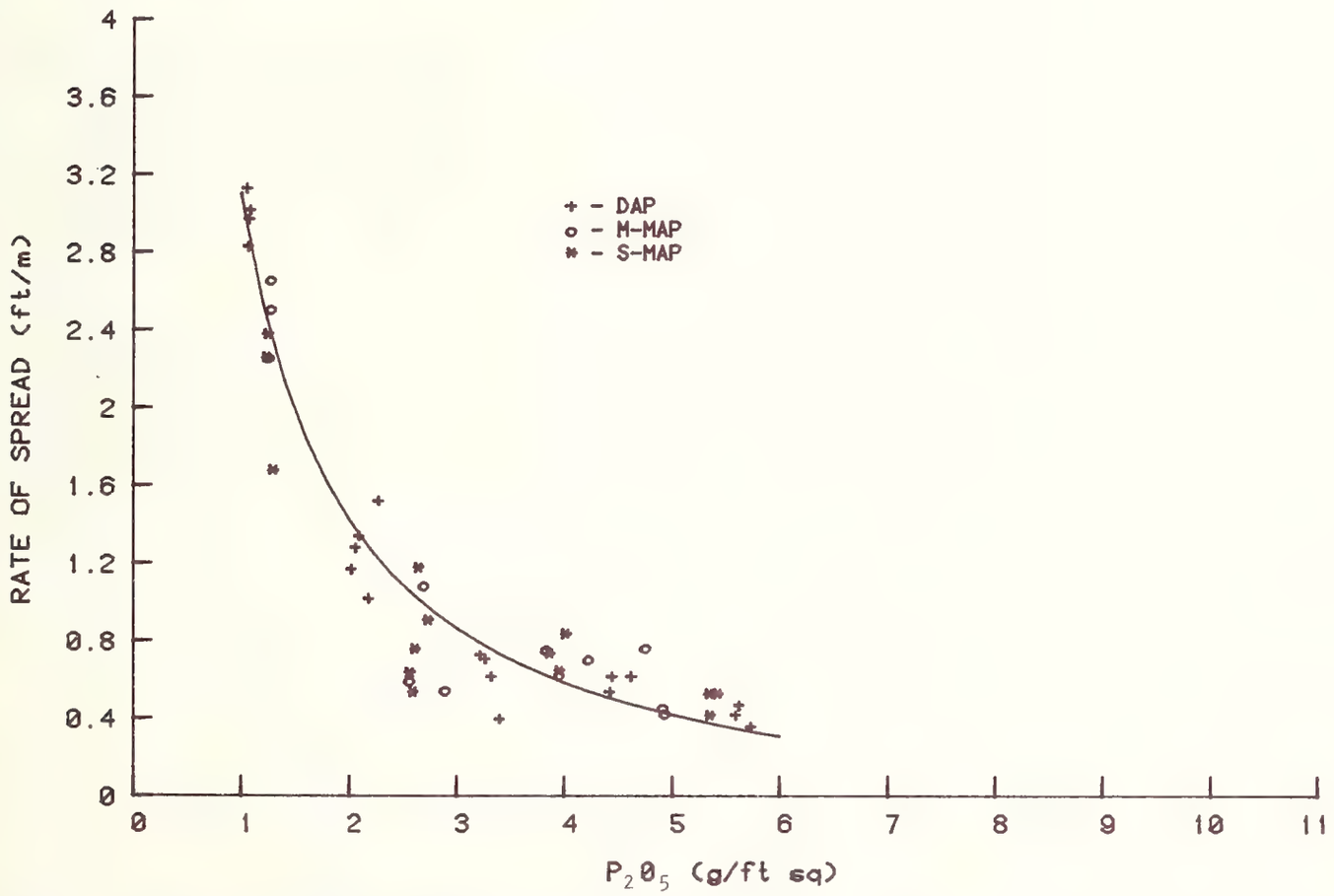

Figure 3.—Effect of DAP, M-MAP, and S-MAP on spread rate of excelsior. (Equation for pooled data is plotted.)

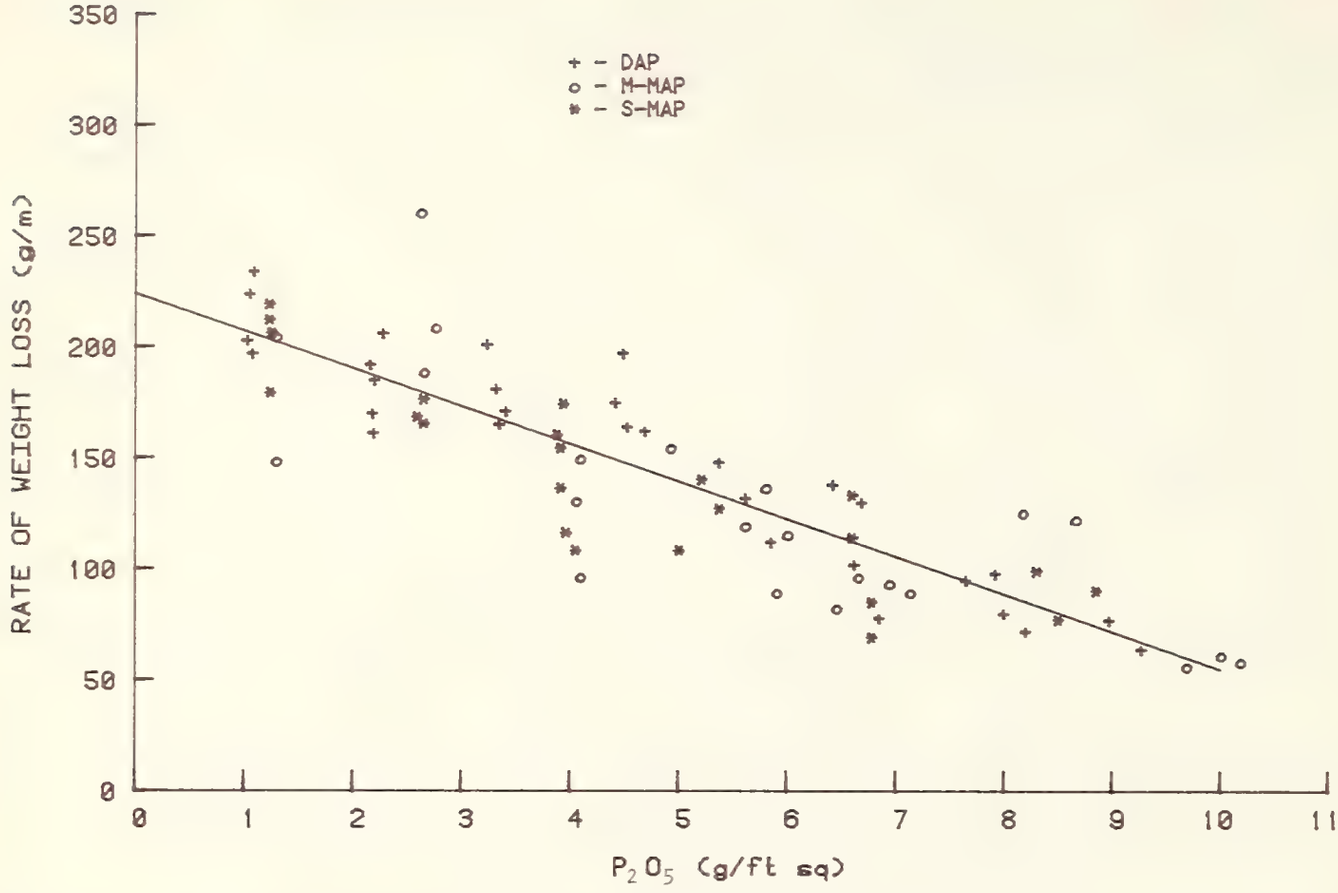

Figure 4.—Effect of DAP, M-MAP, and S-MAP on weight loss rate of pine needles. (Equation for pooled data is plotted.)

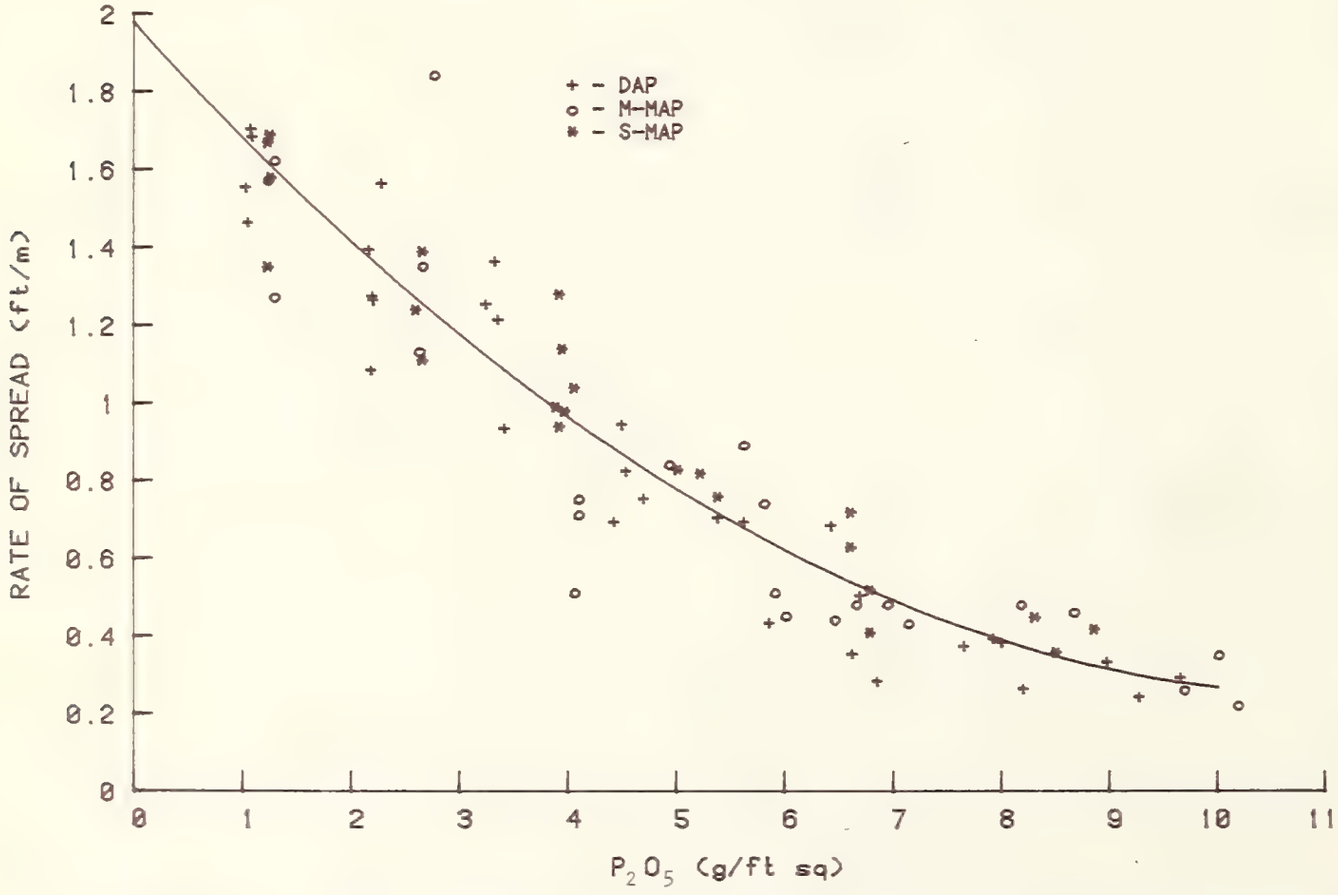

Figure 5.—Effect of DAP, M-MAP, and S-MAP on spread rate of pine needles. (Equation for pooled data is plotted.)

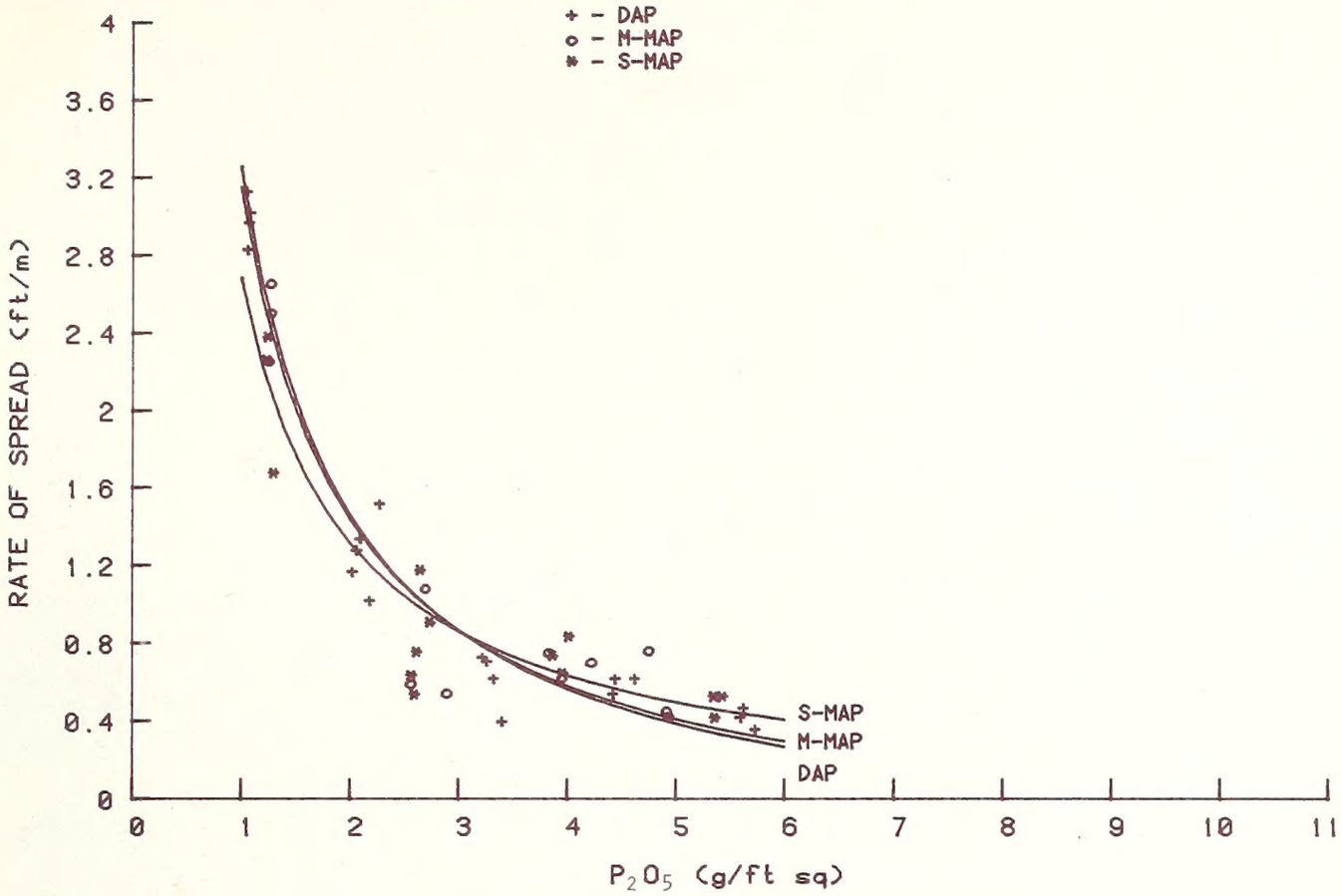

Figure 6.—Effect of DAP, M-MAP, and S-MAP on spread rate of excelsior.

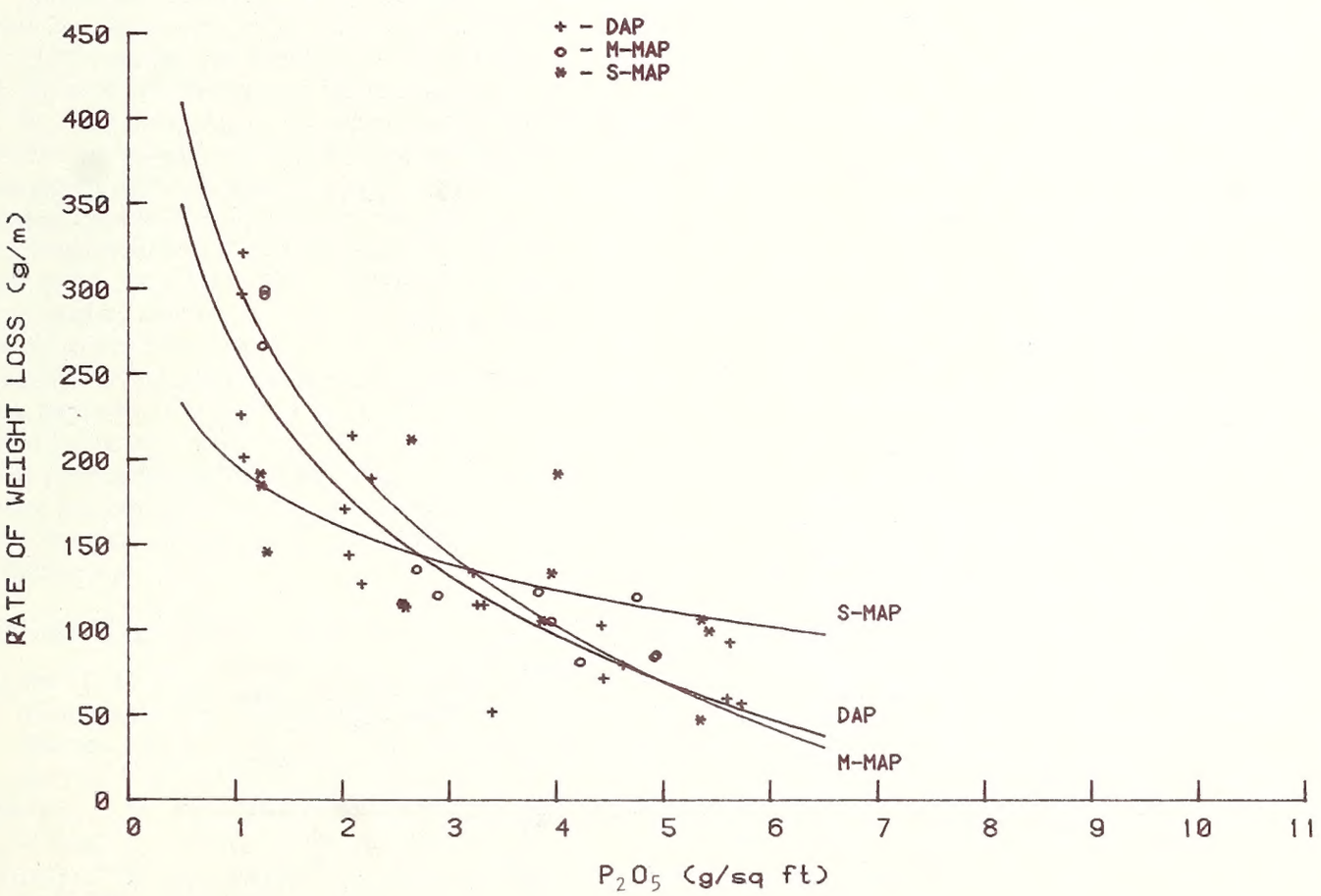

Figure 7.—Effect of DAP, M-MAP, and S-MAP on weight loss rate of excelsior.

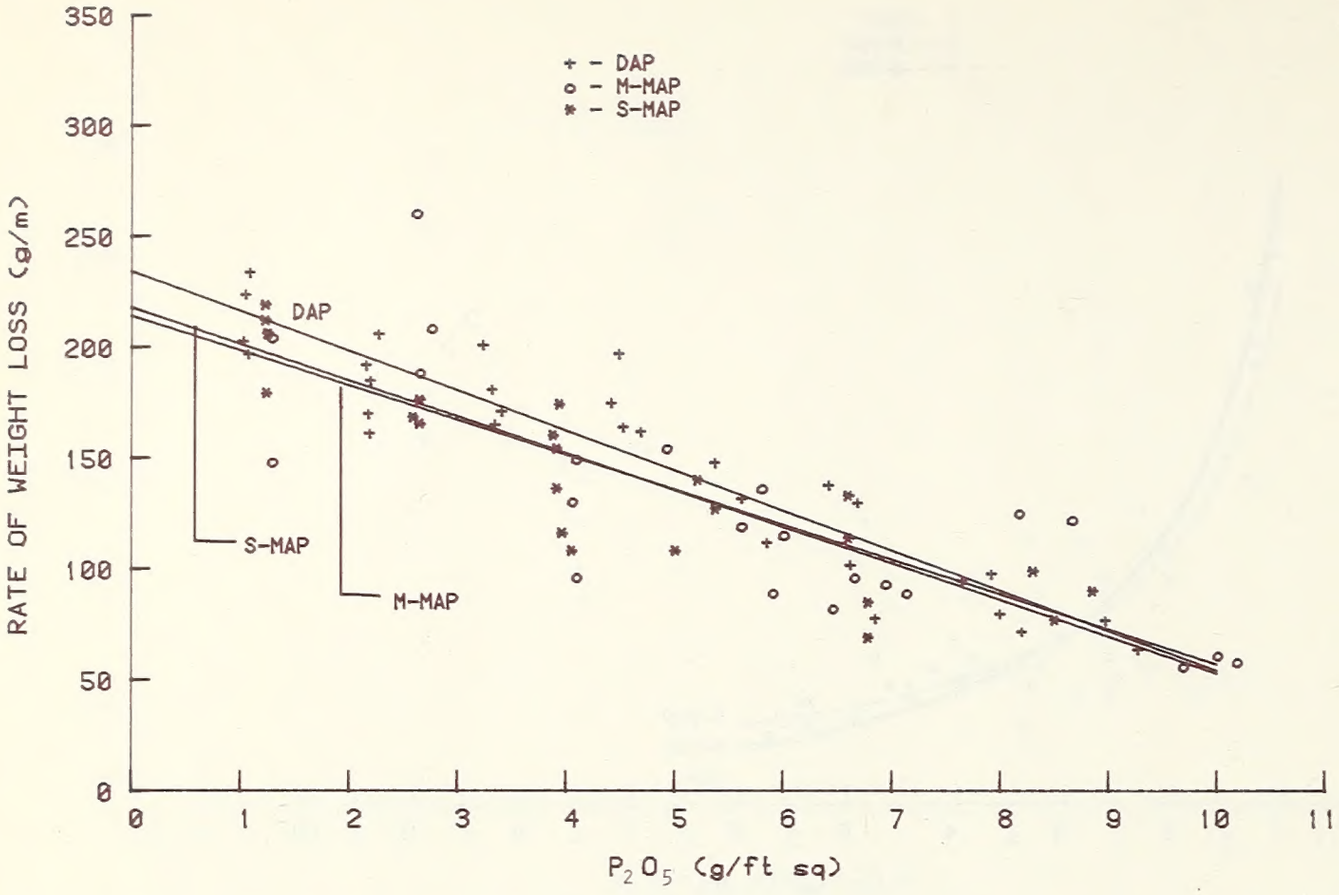

Figure 8.—Effect of DAP, M-MAP, and S-MAP on weight loss rate of pine needles.

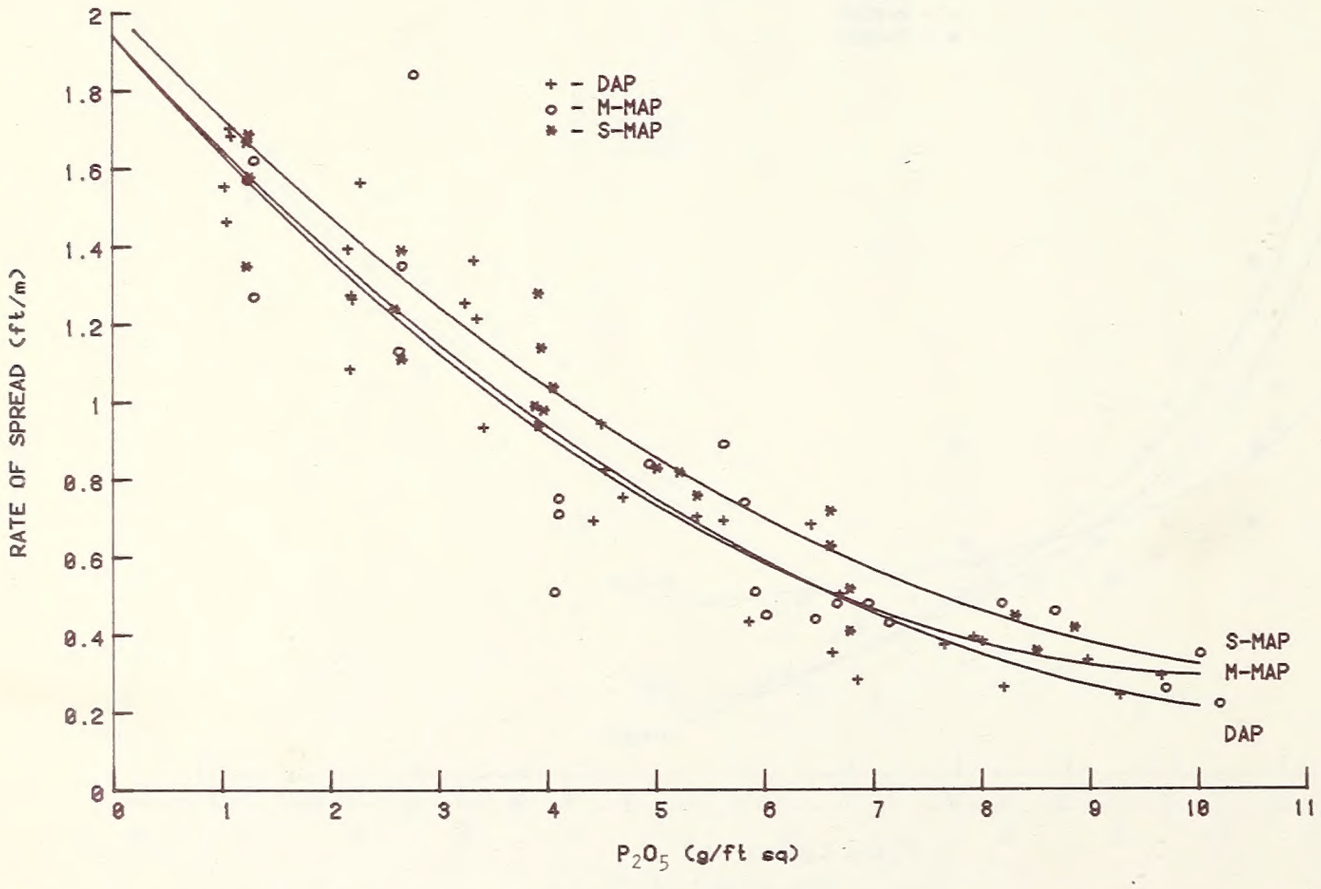

Figure 9.—Effect of DAP, M-MAP, and S-MAP on spread rate of pine needles.

SUMMARY AND DISCUSSION

The study objective was to compare the fire-retarding effectiveness of diammonium phosphate and several samples of monoammonium phosphate. Diammonium phosphate has been the standard for several years; therefore, the other chemicals were compared to its effectiveness. M-MAP and S-MAP proved to be as effective as DAP for retarding flaming and glowing combustion when compared on an equal P_2O_5 equivalent basis under statistical analysis. The other three samples—D-MAP, A-MAP, and T-MAP—(even though fewer burning tests were performed) appear to be equally as effective. The differences in flammability reduction are because of experimental error and are not statistically significant. They are probably caused by inconsistencies and variations in fuel bed construction, fuel physical configuration, fuel moisture content, environmental conditions, and so forth.

These tests and others (George and Susott 1971) indicate that the most important chemical characteristic is the available phosphorus (P). As the chemical is heated, the phosphate (PO_4) compounds are converted to phosphoric acid (H_3PO_4) that alters pyrolysis of the fuel. Both diammonium and monoammonium phosphates are converted easily to H_3PO_4because the ammonia cations (NH_3) are driven off at low temperature:

$$(NH_4)_2\,HPO_4 \xrightarrow[\Delta]{166^\circ\,C} NH_4\,H_2PO_4 + NH_3\uparrow$$

$$\xrightarrow[\Delta]{190^\circ\,C} H_3PO_4 + NH_3\uparrow \rightarrow H_2O + P_2O_5$$

Phosphate anions (PO_4), when combined with sodium (Na), calcium (Ca), potassium (K), and others, cannot be converted to H_3PO_4 readily, and therefore do not make the PO_4 available in the most effective form as fire retardant.

Whether or not one or two ammonias are associated with the P does not appear to make a difference. The method for associating the ammonia with the phosphate (PO_4) also does not appear to affect the fire-retardant ability. Whether ammonia is extracted from coal smoke that is being "scrubbed" with phosphoric acid (D-MAP) or whether the acid is being ammoniated by bubbling ammonia gas into it (S- and T-MAP) seems to make no difference in the availability of P and the resulting fire-retarding effectiveness. A-MAP, produced from a less pure acid, is as effective as the other MAP forms when most of the impurities have been removed after ammoniation. The fire-retarding effectiveness of each MAP (and also DAP), when in a pure form, can be equated on the P or P_2O_5 content. Any formulations containing impurities may change the level of effectiveness.

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The study quantified differences between fire-retarding abilities of monoammonium phosphate samples from five different sources. Ponderosa pine needles and aspen excelsior fuel beds were spray-treated with different levels of chemical solutions, dried, and burned under controlled laboratory conditions. Flame spread and energy release rates were used for comparisons. All five monoammonium phosphate samples proved to be equally effective.

KEYWORDS: forest fire retardent, ammonium phosphate, monoammonium phosphate, flame spread rate, energy release rate, chemical manufacturing method

The Intermountain Station, headquartered in Ogden, Utah, is one of eight regional experiment stations charged with providing scientific knowledge to help resource managers meet human needs and protect forest and range ecosystems.

The Intermountain Station includes the States of Montana, Idaho, Utah, Nevada, and western Wyoming. About 231 million acres, or 85 percent, of the land area in the Station territory are classified as forest and rangeland. These lands include grasslands, deserts, shrublands, alpine areas, and well-stocked forests. They supply fiber for forest industries; minerals for energy and industrial development; and water for domestic and industrial consumption. They also provide recreation opportunities for millions of visitors each year.

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