FIRE-RETARDING COATINGS

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FIRE-RETARDING COATINGS

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Protection of wood against the spreading of fire can be provided by two types of treatments, impregnation with fire-retarding chemicals and surface coverings of fire-retarding coatings. Impregnated wood has been in use to a limited extent for many years and during the war years, large quantities were used in the construction of military installations. It is an established commodity. Fire-retarding coatings, on the other hand, have received little recognition principally because of the lack of standards for minimum requirements enabling the purchaser to know whether he was purchasing a good product or one of little or no merit. The Forest Products Laboratory has been interested for some time in the possibilities of fire-retarding coatings to check the spread of small fires and has made many fire tests of the effectiveness of such materials. This report outlines what can be expected in the way of protection from a number of fire-retarding coating formulations and contains information on the properties of such preparations.

Wood exposed to fire temperatures will char, regardless of whether it is coated or not. The best that can be expected of a paint-type coating is to stop or retard the spread of flame along the surface. The degree to which flame spread is checked is dependent on the type of coating and its thickness and on the fire conditions present, such as design of the painted structure, size of the fire, duration of exposure, presence of draft, and temperature of the air. After fires develop to large size and burn rapidly or for considerable periods, they may overcome the resistance of fire-retarding coatings; but small fires can often be kept small or even caused to die out by suitable coatings.

Various tests have been devised to measure the effectiveness of fire-retarding coatings in checking flame spread under varying conditions of fire severity, but the work done has been insufficient to determine how effective such coatings are in actual use. The Laboratory has used the fire-tube test[2] for much of its fire-testing work. In this test, a specimen measuring 40 inches by 3/4 inch by 3/8 inch is suspended vertically within a sheet-iron cylinder 3 inches in diameter, and a Bunsen burner with an 11-inch flame is placed beneath the specimen. The percentage loss in weight of the specimen

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[1] Maintained at Madison, Wisconsin, in cooperation with the University of Wisconsin.

[2] Details of this and other test methods are given in Report No. R1443.

is recorded at intervals of 30 seconds. At the end of 4 minutes the burner is removed, but percent losses in weight are recorded until burning ceases. In this test, untreated or uncoated wood loses about 50 percent of its weight after a 3-minute exposure to the flame and 70 percent or more of its weight is gone when blazing and glowing cease. In evaluating the degree of protection afforded by coatings, a loss of weight of less than 30 percent after an exposure of 3 minutes is considered to indicate protection against mild fires, whereas a final loss of weight of less than 25 percent is considered to indicate protection against fires of considerably greater severity.

Another method of test being used is a modification of one developed by Ragnar Schlyter of the Swedish Government Testing Institute. In this method two test panels, 12 inches by 31 inches by 3/8 inch, are stood in a vertical position, parallel to each other and 2 inches apart, with the bottom of one panel 4 inches above that of the other. Either a wing-top Bunsen burner flame (mild test) or the flame from a Meker burner provided with a special "T" head (severe test) is placed between the two panels and readings are taken of the vertical progress of the flame spread with time. With unprotected wood, the flame will spread over the surfaces and destroy the specimens, but with effective fire-retarding coatings on the exposed surfaces the flame ceases to spread as soon as the gas burner is removed.

The Forest Products Laboratory has used the foregoing methods together with several others to study the performance of a large number of formulations in its efforts to find good fire retardants and to determine their ability to provide good protection with a reasonable number of coats. In addition to fire-retarding effectiveness, other properties must be taken into consideration. Among these are reasonable permanence of both fire-retarding effectiveness and adherence of coating to the wood, resistance to comparatively high relative humidity, and, to some extent, the appearance of the coating. Resistance to weather is also desirable but is usually absent.

On the basis of the examination of numerous coatings, the Laboratory has drawn the following conclusions regarding certain types of preparations tested.

Borax-linseed Oil Fire-retardant Paints

Linseed-oil-base paints of good fire-retarding effectiveness can be made by replacing an appreciable portion of the pigment with finely ground borax. The percentage of borax required varies with the kind of pigment. The following table gives four examples of single pigment formulations, heavy coats of which were found to provide sufficient protection to keep the final loss in weight in the fire-tube test under 25 percent; 3 or 4 thick coats or approximately 1 gallon per 125 square feet are required.

Coatings of ordinary thickness undoubtedly would provide protection against comparatively weak fires, but for highest resistance thick coatings must be used. This type of paint is good for interior use from the

standpoints of appearance, moderate moisture resistance, and permanence. It will not retain its effectiveness, however, after repeated exposure to rain and for that reason it is not suitable for outdoor use.

Borax-linseed oil fire-retardant paint formulas

Pigment	Formula (1)	Formula (2)	Formula (3)	Formula (4)
	Percent by weight			
White lead[1]	41.0			
Titanium-calcium		30.0		
Lithopone			24.0	
Zinc oxide				21.0
Borax	32.0	35.0	39.5	50.0
Raw linseed oil	22.8	30.8	32.3	24.8
Turpentine	3.6	3.6	3.6	3.6
Japan drier	.6	.6	.6	.6

[1]Basic carbonate white lead.

Water Solutions of Fire-retarding Chemicals

Sodium silicate

Sodium silicate is an excellent fire retardant when freshly applied. Very good protection is furnished for a limited time by three coats of the commercial viscous syrup (water glass) diluted with a minimum quantity of water necessary to give a liquid of suitable brushing consistency. The addition of a small quantity of liquid soap or other wetting agent improves the wetting properties of the silicate solution. Moderate protection is furnished by two coats.

Sodium silicate is available in a number of grades based on the soda-silica ratio. The grades with a high silica ratio are preferred for fire-retarding coatings.

The serious weakness of sodium silicate coatings is their instability. A series of tests on fire-tube specimens coated with various silicate formulations and exposed to different relative humidity conditions revealed the following: Exposure to a relative humidity of 65 percent at 80° F. caused a serious decrease in effectiveness after only one month and a relative humidity of 90 percent at 80° F. caused the high silica-ratio coatings to check, crack, and peel. Under similar conditions, low silica-ratio compositions became soft and sometimes dripped. In dry situations, the

effectiveness continued over a much longer period, being retained under favorable conditions for more than a year; but it is seldom that use conditions are such that high humidities are always avoided.

The fire protection given by sodium silicate is largely due to its property of intumescence; that is, the coating when exposed to heat swells to a frothy mass that hardens and thus insulates the wood against heat. The property of intumescence is absent in silicate coatings that have been exposed to high relative humidities; this seems to account for the decrease in effectiveness of silicate coatings after such exposures. The explanation given for the decrease in effectiveness with time, especially under high moisture conditions, is that the carbon dioxide of the air in the presence of moisture reacts with the sodium silicate to convert it to sodium carbonate and silica, neither of which intumesce on exposure to heat.

The inclusion of pigments in the silicate formulations improves the appearance and brushing properties of the preparations. The British[3] recommend such a pigmented sodium silicate preparation for the protection of wood in attics against incendiary-bomb fires. The British formula is:

Sodium silicate solution (Specific gravity 1.41 to 1.42 Silica-soda ratio 3.2 to 3.4)	- 112 lbs.	(5)
Kaolin	- 150 lbs.	
Water	- 100 lbs.	

Three to 4 coats of this preparation are required to give good protection. One gallon will cover approximately 100 square feet (4 coats).

Ammonium phosphate and other fire-retarding chemicals

Strong solutions (25 percent or higher) of such good fire-retarding chemicals as monoammonium phosphate, diammonium phosphate, a mixture of ammonium sulfate and monoammonium phosphate, and a high-solubility mixture of borax and boric acid have fire-retarding properties when applied to wood. These solutions, however, are not syrupy, as is water glass, and the quantity of dry chemical that can be applied per coat is so small that an unpractical number of coats is necessary to build up the coating weight sufficiently to give protection comparable to that obtained with 3 to 4 coats of borax-linseed oil paint or 2 to 3 coats of sodium silicate. Nevertheless, 3 coats of saturated solutions of good fire-retarding chemicals do have definite, although moderate, fire-retarding effectiveness.

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[3] British Standards Air Raid Precaution Series 39, February 1940.

Preparations Formulated with Thickening Agents

As stated in the preceding paragraph, the weakness of simple water solutions of fire-retarding chemicals for use as coatings is the comparatively small quantity of chemical that can be applied per coat. This weakness can be overcome to a considerable extent through the use of a thickening agent in the formulation. Two materials of this type that are of value in fire-retarding formulations are sodium alginate and methyl cellulose. Two-percent solutions of these wetting agents are viscous gels.

Alginate preparations

No chemical reaction occurs between sodium alginate and ammonium fire-retardant salts. Borax causes the gel to set, but boric acid and mixtures of boric acid and borax are compatible with the gel. The best formulations thus far prepared, considered from all angles, contain monoammonium phosphate, but fairly satisfactory preparations can be made from a mixture of borax and boric acid. Preparations can be made either with a strong solution of the chemical or with the finely ground fire-retardant chemical dissolved and suspended in the aqueous gel. Pigments also may be introduced into such preparations.

Four of the methods that have been used for preparing typical ammonium phosphate formulas are as follows:

Method I

	Parts by weight	
Monoammonium phosphate	50	
Two percent sodium alginate gel	50	(6)

1. Prepare the alginate gel by adding 2 parts by weight of sodium alginate to 98 parts of hot water. Stir until a uniform gel is obtained.

2. Grind in a pebble mill equal parts by weight of monoammonium phosphate and alginate gel. A grinding period of 12 to 24 hours is sufficient.

Method II

	Parts by weight	
Monoammonium phosphate	50	
Titanium dioxide	5	(7)
Two percent sodium alginate gel	45	

1. Prepare alginate gel.

2. Grind monoammonium phosphate and titanium dioxide together in a pebble mill until the material is reduced to approximately 200 mesh.

3. Mix in a blade mixer 55 parts by weight of the phosphate-titanium dioxide powder and 45 parts by weight of the alginate gel until a uniform preparation is obtained.

The purpose of the titanium dioxide is to facilitate grinding and prevent lumping of the ammonium phosphate in storage and to give the coating better hiding power. Inclusion of the titanium dioxide also improves the brushing properties of the paint and produces a coating somewhat finer grained than a pure ammonium phosphate coating.

Method III

	Parts by weight	
Monoammonium phosphate	88.5	
China clay	10.0	(8)
Dry sodium alginate	1.5	

1. Grind sodium alginate to 325 mesh.

2. Grind the prescribed quantities of monoammonium phosphate, china clay, and powdered sodium alginate until the particle size of the ammonium phosphate is approximately 200 mesh.

This procedure will produce a powder similar to calcimine or dry casein paint. To prepare it for use, add 4 to 5 parts by weight of water to 6 parts by weight of the powder and stir until the powder is mixed thoroughly with the water. Allow to stand for at least an hour and stir again until a smooth mixture is obtained.

Method IV

	Parts by weight	
Monoammonium phosphate	25	(9)
Two percent sodium alginate gel	75	

1. Prepare the alginate gel by adding 2 parts by weight of sodium alginate to 98 parts of hot water. Stir until a uniform gel is obtained.

2. After a uniform gel is produced, dissolve 1 part by weight of monoammonium phosphate in 3 parts of the alginate gel.

Of the four phosphate formulas, formula 9 is the simplest to prepare since it requires no special equipment. Since its content of ammonium phosphate, however, is less than that of formulas 6, 7, and 8, more coats of it are required than of the other three to give the same degree of protection.

The properties of preparations with monoammonium phosphate in suspension (formulas 6, 7, and 8) may be summarized as follows:

The paints have good brushing properties, producing smooth coats. The solids remain in suspension during application and, although they settle after standing for some time, can be returned to suspension very readily by stirring. The preparations are stable for an indefinite period so far as is known. Solutions of monoammonium phosphate are corrosive to many metals. If the paints are packaged in uncoated metal containers or are to be applied by spray-gun, the addition of the corrosion inhibitor, sodium dichromate, is desirable. Two to 3 percent of the ammonium phosphate content is sufficient. The body of the preparations is such that sufficient dry fire retardant can be applied in 2 or 3 coats to give sufficient protection to keep the final loss in weight, as measured by the fire-tube, under 25 percent. Heavy coats of these preparations stopped the spread of fire in the severe Schlyter test and in tests involving the high temperatures developed by different types of incendiary bombs. The coverage per gallon is approximately 70 square feet for 3 coats.

The coatings on drying are flat white, resembling casein paints or calcimine. Their adherence to wood is good. Relative humidities up to 91 percent have no effect upon monoammonium phosphate, but at humidities higher than this, the phosphate takes on water. Under ordinary conditions, the fire-retarding effectiveness should be retained indefinitely.

Methods I and II can be used to prepare such borate formulations as the following:

	Parts by weight	
	Formula (10)	Formula (11)
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	32.5	----
Boric acid	32.5	37.5
Two percent alginate gel	35	62.5

The procedure of Method III can be used satisfactorily to prepare dry-mix powders consisting of boric acid and dry sodium alginate. Dry-mix powders containing borax and boric acid can be prepared, however, only by using a partially dehydrated borax. The grade of borax most commonly sold, containing 47 percent of water of crystallization, is not satisfactory for preparations of this type because a reaction occurs between it and boric acid in which sufficient water is liberated to cause the mixture to become damp and to pack. If the borax is dehydrated sufficiently, satisfactory dry mixes can be prepared. Examples of dry-mix borate preparations are:

	Parts by weight	
	Formula (12)	Formula (13)
Boric acid	98	60
Borax (82% $Na_2B_4O_7$	--	38
Dry sodium alginate	2	2

The borate coatings do not have such good fire-retarding effectiveness as the phosphate coatings on an equal weight basis, so that it is necessary to use them in slightly heavier coats to obtain the same effectiveness. Neither is the adherence to wood of this type of coating as uniformly satisfactory as that of the phosphate coatings. In some cases adherence has been excellent after a year's exposure to outside weather conditions, protected against rain. In other cases under interior exposure conditions, the coatings have peeled from the wood after a comparatively short time. The borate coatings, especially those containing only boric acid withstand very high relative humidities better than do the ammonium phosphate coatings. However, considering all factors, the monoammonium phosphate type is more dependable than the borate type.

The formulations given are illustrative of moderately heavy-bodied preparations. If still heavier-bodied paints suitable for trowelling or coarse spray are desired, they can be prepared by increasing the percentage of solids. If thinner mixtures are desired, they can be made by decreasing the percentage of solids or using a less viscous alginate gel. Likewise, if colored paints are desired, they can be made by substituting suitable pigments for the china clay.

Methyl Cellulose Preparations

Methyl cellulose is a thickening agent that can be used to prepare paints with properties similar to those described under alginate preparations. It is suitable for use with borax, boric acid, and mixtures of borax and boric acid, but it cannot be used with ammonium phosphate, as it is coagulated by this salt in the high concentrations used in fire-retarding preparations. The material is furnished in several viscosity grades. In the experimental formulations tested, the grades capable of producing viscous solutions with a minimum quantity of material have been used.

Typical formulations together with the method of preparation are as follows:

	Parts by weight		
	Formula (14)	Formula (15)	Formula (16)
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	50	--	30
Boric acid	--	50	30
2% methyl cellulose (1500 c.p.) gel	50	50	40

1. Prepare the methyl cellulose gel as follows: mix 2 parts (by weight) of the methyl cellulose thoroughly with 50 parts of water at boiling temperature, and allow it to soak for 20 to 30 minutes. Add 48 parts of cold water and stir until smooth.

2. Grind in a pebble mill the required quantity of boron compound and of methyl cellulose gel until the mixture is of fine-grained consistency.

The properties of these preparations and of the dry coatings are similar to those of the borate-alginate preparations. Three coats provide sufficient protection to stop the spread of flame in the severe Schlyter test.

Whitewash

Whitewash is generally regarded as having fire-retarding properties. Significant effectiveness cannot, however, be obtained with a one-coat application. The following two whitewash formulations that were tested gave moderate protection when three coats were applied:

National Fire Protection Handbook (8th edition) formula - page 424.

Mix together 10 parts slaked lime, 1 part of Portland cement, and sufficient salt water to give a mixture of rather stiff consistency. (17)

(Bulletin No. 304-D, Formula 9, - National Lime Association)

Casein - 5 lbs.
Borax - 3 lbs. (18)
Lime paste - 8 gals. (Approximately 8 gallons of stiff lime paste are produced by slaking 25 pounds of quicklime with 10 gallons of water, or by soaking 50 pounds of hydrated lime in 6 gallons of water.)

Directions as given by the association: "Soak the casein in 4 gallons of hot water until thoroughly softened (about 2 hours). Dissolve the borax in 2 gallons of water and add this solution to the casein. When both are cold, slowly add the borax-casein solution to the lime paste, stirring constantly and vigorously. Thin to desired consistency. Do not prepare a larger quantity of this formula than can be used in a day, as it may deteriorate."

Tests made at the Laboratory show that neither the adherence nor the fire-retarding effectiveness of whitewash (formula 18) is seriously affected by exposure of several months to a relative humidity of 90 percent at 80° F.

Casein Paints

Casein paints possess moderate fire-retarding effectiveness if at least three coats are applied. The effectiveness is increased if borax is introduced into the formula.

The degree of fire protection provided by three coats of whitewash or casein paint is by no means comparable with that provided by three coats of borax-linseed oil paint, sodium silicate, or the phosphate-alginate preparations.

Magnesium Oxychloride and Magnesium Oxysulfate Coatings

Preparations of this type made by mixing magnesium oxide (magnesite) with a solution of either magnesium chloride or magnesium sulfate provide good protection when applied in heavy coats (100 grams of dry coating per square foot). The only formulations tested were proprietary. The best of those tested adhered reasonably well to wood, but some showed a strong tendency to flake off, especially when applied in heavy coats.

Synthetic-resin Formulations

Certain combinations of urea-formaldehyde resins and ammonium phosphate provide excellent protection. The coating owes its effectiveness to the intumescence of the resin on exposure to heat and the protection against combustion of the charred frothy mass by the ammonium phosphate present.

Water-insoluble Fire-retardant Preparations

A major weakness of the fire-retardant coatings discussed in this paper is their inability to retain their effectiveness after exposure to water, due to the removal of the water-soluble fire retardant. So far as is known, no water-insoluble compound has been found equal in effectiveness to such water-soluble compounds as ammonium phosphate, borax, and sodium silicate. Water-insoluble compounds having fire-retardant properties are zinc borate, chlorinated rubber, and chlorinated paraffin.

Zinc Borate

Formulation (19), when applied in heavy coats, provides sufficient protection to check flame spread under the conditions of the mild Schlyter test.

	Percent by weight	
Zinc borate	30.0	
Basic carbonate white lead	34.3	
Raw linseed oil	31.6	(19)
Turpentine	3.5	
Drier	.6	

Chlorinated Rubber

This compound, if applied in coating weights of 25 grams or more per square foot, provides protection to wood against fires of a mild or moderate degree of severity.

Chlorinated Paraffin

This compound is the basis of a number of exterior fire-retarding paints. The formulations vary in the degree of protection against flame spread they provide, from slight to moderate effectiveness.

Loose-texture Compositions

Certain compositions applied by spray gun in a thickness of one-half to 1 inch are in use for heat insulation purposes. These coatings contain such materials as mineral wool, asbestos, or shredded cellulosic materials treated with fire-retarding chemicals, with only sufficient binder to hold the mass loosely together. Such coatings have good fire-retarding properties and are useful where a combination heat-insulating, fire-retarding preparation is desired. Coatings of such compositions thinner than those necessary for heat insulation purposes possess sufficient fire retardance to be useful for fire protection only. The soft, spongy nature of these coatings limit their use for fire protection to such applications as ceilings and attics, or other places where resistance to wear is not required. The adherence of certain types of this material to laboratory-size specimens of wood was not good, expecially under fire conditions, but how serious this defect would be on large installations under fire conditions is not known.