Development and Evaluation of Fire Retardant Coatings

Dr. N. K. Saxena* and Dr. D. R. Gupta**

Abstract

A few fire retardant intumescent coatings based on ammonium phosphate, cyanoguanidine, 2- 2 bis hydroxymethyl 1,3-propanediol (polyol), and a binder (a copolymer of vinyl acetate acrylate copolymer emulsion and an amino resin) have been developed for wood and wood-based products. The fire performance of the coatings has been evaluated employing differing BS and ASTM standards. On exposure, the coated specimens neither show any surface spread of flame nor any afterglow combustion. The coatings are found to be quite effective in reducing smoke generation, and they possess good water repellency and adhesion.

Introduction

Wood and wood-based panel products, i.e. plywood, particle boards, fiber boards, etc., are extensively used in buildings for doors, windows, partitions, and thermal and acoustical treatments as well as for decorative purposes. These materials are highly combustible and often pose fire hazards. If these materials are suitably treated for fire retardance, they will not only decrease the growth period of fire but will also reduce the spread of flame thereby obviating fire hazards and loss of life and property.

In order to retard the ignition and surface spread of flame on these materials, different techniques such as chemical impregnation, surface treatment, spray, and incorporation of fire retardants during the product manufacture are often used.[1] There are two types of coatings that retard the spread of fire. One type of coating, called a fire retardant coating, uses additives such as borax, boric acid, antimony trioxide, and chlori-

*Fire Research Laboratory, Central Building Research Institute, Roorkee, India

**Professor, Department of Chemistry, University of Roorkee, Roorkee, India

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nated compounds,[2-6] which do not support combustion. The other type is called an intumescent coating, which, when heated produces residues that are puffed up or are swelled by escaping gases. A combustion residue can be efficiently puffed up in order to produce a tough insulating foam over the surfaces to protect the material.[6-9] These coatings perform better than fire retardant coatings. This paper is concerned with the development and evaluation of a few fire retardant intumescent coatings.

Experimental

Materials and Method

The binders used were obtained from Calico Chemicals Ltd., Bombay; Parekh Dyechem Industries Pvt. Ltd., Bombay; and Synthetic and Polymer Industries, Ahmedabad.

Fire retardant intumescent coatings were prepared using binders and fire retardant ingredients. The compositions are given in Table 1. The coatings were prepared by mixing fire retardant ingredients of 325-400 mesh size with a 2 percent solution of sodium salt of d-mannuronic acid and an appropriate binder. A requisite amount of water was added in order to obtain brush consistency. Characteristics of these coatings, like density, covering capacity, and solid binder ratio, were determined and are listed in Table 2. The paints were applied by brush on combustible surfaces of plywood, wood, hard board, and fiber board. For obtaining effective fire retardancy, the thickness of the paint film was maintained

Table 1: Compositions of Fire Retardant Intumescent Coatings

	Parts by Weight for Formulation Nos.						
Ingredients	1	2	3	4	5	6	7
Ammonium Phosphate	24	25	25	35	25	24	24
Cyanoguanidine/Dicyandiamide	14	-	20	-	20	14	14
Urea	-	-	-	15	-	-	-
Melamine	-	15	-		-	-	-
Polyol	10	10	10	10	10	10	10
Paraformaldehyde	03	05	03	03	03	03	03
Titanium dioxide	3.2	03	03	03	03	3.2	03
Sodium salt of d-mannuronic acid (2% soln.)	22	22	20	22	20	22	22
Binders:							
Calimul 6825	16	17	-	20	-	16	11
Pidivyl C. P. 651	-	-	19	-	-	-	-
Rollex-50	-	-	-	-	17	05	05
Water	7.8	08	10	10	07	7.8	7.8

Table 2: Physical Properties of Coatings

Composition No.	Density gms/cc	Covering Capacity at Rate of 280 gm Active Ingredients/m²	Solid-binder Ratio
1	1.30	1.82	5.99
2	1.30	1.96	6.03
3	1.30	2.07	5.77
4	1.32	2.23	5.82
5	1.35	2.07	7.67
6	1.28	1.82	4.70
7	1.27	1.90	6.27

at 10-12 mil by applying fire retardant active ingredients at the rate of 280 gms/m^2. The surfaces of the materials were rendered water repellent by applying a coat of a copolymer of VC/VA (Caliplast 613) in ethyl acetate at the rate of 220 ml/m^2.

Testing and Evaluation of Coatings

The flame spread rate, afterglow combustion, char volume, and weight loss of the coatings were evaluated by standard procedures.

Fire Retardancy of Paints (Cabinet Method ASTM D-1360)

After subjecting the specimens to a flame, weight loss and char volume were determined.[10] The apparatus consisted of a metal cabinet with a sliding shutter of glass. Inside the cabinet, there was a supporting frame for the test panels and the solvent cup. Weighed panels (6 × 150 × 305 mm), free from knots and other imperfections were used employing ethyl alcohol (5 ml) as an ignition fuel. The test was continued until the flames were extinguished. The burning test data for the control and the coated specimens are given in Table 3.

*Table 3: Performance of Intumescent Coating on Mango Wood (6 mm)**

Comp. No.	Flame Sprd. (Sec.)	Afterglow (Sec.)Loss	Avg. Wt. (gms)	Avg. Char Vol. (C.C.)	Hgt. of Intum-escence (mm)
1	0	0	2.25	0	17
2	0	0	2.42	0	17
3	0	0	2.30	0	17
4	0	0	2.34	0	12
5	0	0	2.24	0	10
6	0	0	3.06	0	10
7	0	0	2.26	0	14
Control	42	Contd.	21.12	50.40	-

*ASTM D-1360

Table 4: Output of Radiometer

Dist. from hotter end of specimen (mm)	75	150	225	300	375	450	525	600	675	750	825
Radiant Intensity (Kw/M^2)	37.0	31.0	25.5	21.0	18.4	15.1	13.4	11.7	10.5	8.8	7.5
E.m.f.(mv)	31.5	28.5	26.0	23.5	21.5	19.5	18.0	16.5	15.0	13.5	12.0

Large Scale Surface Spread of Flame Test (BS 476 Part 7)

The apparatus consisted of a vertically mounted gas-fired radiant panel about 900 mm^2. Perpendicular to one side of the radiant panel at its midpoint was a frame arranged to hold a 230 × 900 mm specimen with its long axis horizontal. A small gas flame was located at the intersection of the specimen and the radiant panel. With this arrangement, the intensity of the heat on the specimen decreases as its distance from the radiant panel increases (see Table 4). A 75 mm to 100 mm long vertical gas flame was applied to the hotter end of the specimen for one minute, immediately after the specimen was placed in test position. On the basis of observed behavior under test, specimens were classified[11] as given in Table 5. Observations were made of the time of the spread of flame front for measured distances along the specimen, until the flames died out or for 10 minutes, whichever was longer. Test data are recorded in Table 6.

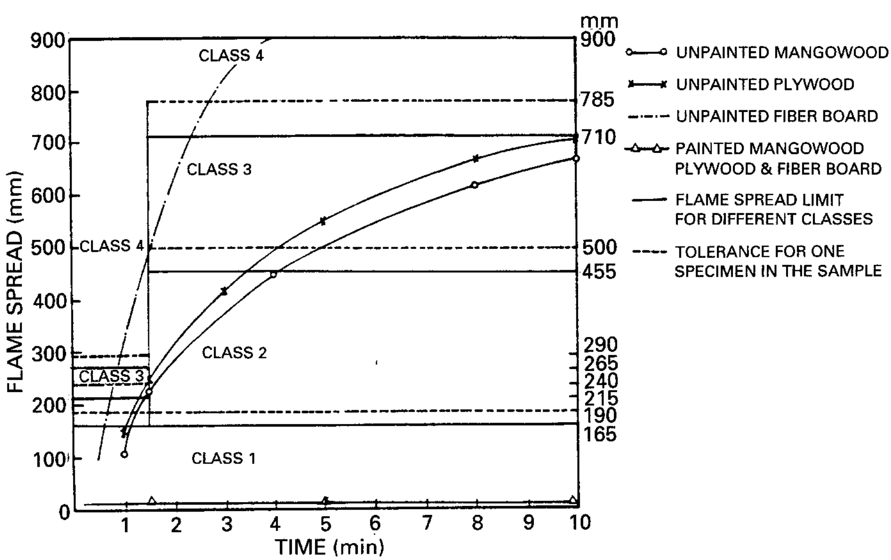

Figure 1: Surface Spread of Flame Test on Wood.

Table 5: Flame Spread Classification

Classification	Flame spread at 1.5 (min) Limit (mm)	Flame spread at 1.5 (min) Tolerance for one specimen in sample	Final flame spread at 10(min) Limit (mm)	Final flame spread at 10(min) Tolerance (mm) (mm)
Class 1	165	25	165	25
Class 2	215	25	455	45
Class 3	265	25	710	75
Class 4	Exceeding class 3 limit			

Table 6: Large-scale Surface Spread of Flame Test – Results

Materials: Mango wood (12 mm); Plywood (6 mm); Fiber board (18 mm)

Comp. No.	Flame spread at 1.5 min. (mm)	Final flame spread at 10 min (mm)	Classification
1	0	0	Class-1
2	0	0	Class-1
3	0	0	Class-1
4	0	0	Class-1
5	0	0	Class-1
6	0	0	Class-1
7	0	0	Class-1
Control			
Mango wood	230	675	Class-3
Plywood	250	695	Class-3
Fiber board	525	900	Class-4

Fire Propagation Test (BS 476 Part 6)

In this test, the rate and amount of heat evolved by the specimen was taken into account while it was heated in an enclosed space under prescribed conditions. Specimens of plywood (228×228×4 mm) and celotex board (228×228×18 mm) were coated with fire retardant paints and the index of performance was determined from the following equation:[12]

$$i_1 = \sum_{\frac{1}{2}}^{3} \frac{\theta_m - \theta_c}{10t}, \quad i_2 = \sum_{4}^{10} \frac{\theta_m - \theta_c}{10t}, \quad i_3 = \sum_{12}^{20} \frac{\theta_m - \theta_c}{10t}$$

$$I = i_1 + i_2 + i_3$$

where:

I = index of performance

t = time (min) from the origin at which readings were taken

Θ_m = temperature (°C) of the material at time *t*,
Θ_c = temperature (°C) of the calibration curve at time *t*.

Fire performance of coatings is given in Table 7.

Table 7: Fire Propagation Test – Results

Material	Plywood (4mm)		Fiber board (18mm)	
	Results			
Comp. No.	i_1*	I	i_1	I
1	2.002	12.775	2.334	15.130
2	2.013	12.862	2.339	15.278
3	2.056	12.369	2.352	15.288
4	2.119	13.135	2.456	15.847
5	1.983	12.179	2.310	15.111
6	2.246	13.211	2.493	15.892
7	2.010	12.768	2.340	15.152
Control	10.342	30.591	37.291	69.205

*i_1 Subindex (initial burning only). The lower the numerical value of the index, the better is material.

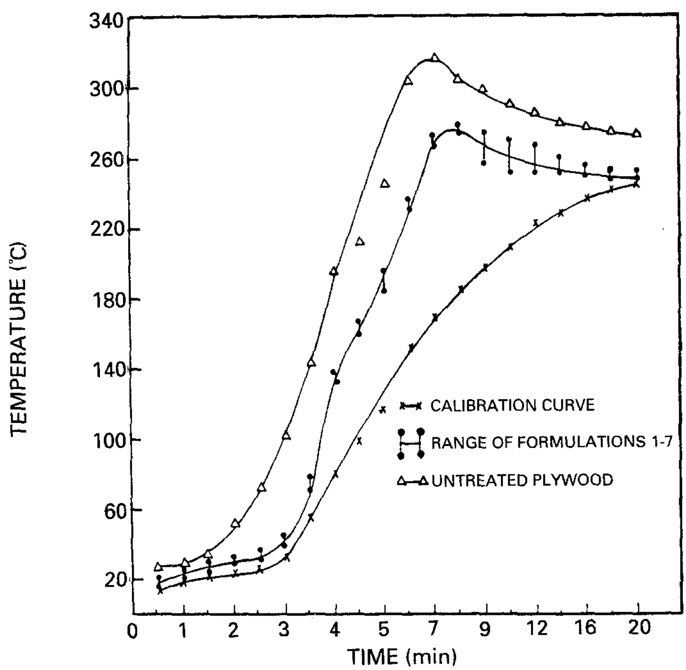

Figure 2: Performance of Paint Formulations on Plywood (as per B.S.476 Pt. 6).

Smoke Generation Test

Tests were carried out in the NBS (National Bureau of Standards) smoke density chamber as described in ASTM E 662.[13] The specimen was arranged to face the electrically heated radiant energy source which is mounted within an insulated ceramic tube and positioned so as to produce an irradiance level of 2.5 w/cm^2 averaged over the central 38.1 mm diameter area of the vertically mounted specimen. A photometric system with a vertical light path was used to measure the varying light transmittance as smoke accumulated. The light transmittance measurements were used to calculate the specific optical density of smoke generated during the time period to reach the maximum value. The tests were stopped when maximum light transmission was reached or after 20 minutes. The following parameters were determined:

D_m = maximum specific optical density
$t_{90\%}$ = moment where upon 90% of D_m is reached (min)
D_{90s} = optical density at 90 sec
SON = sum of specific optical densities at 1 min, 2 min, 3 min, and 4 min, a measure for the rate of smoke development
V_{max} = maximum rate of smoke development estimated every 30 sec and expressed in D_S/min.

SOI (smoke obscuration index) calculated as:

$$\frac{Dm^2}{2000t_{16}}\left(\frac{1}{t_{0.9}-t_{0.7}}+\frac{1}{t_{0.7}-t_{0.5}}+\frac{1}{t_{0.5}-t_{0.3}}+\frac{1}{t_{0.3}-t_{0.1}}\right)$$

where:

t_{16} = time to reach $D_m = 16$
$t_{0.9}, t_{0.7}, t_{0.1}$ = time to reach 90%, 70%....10% of maximum D_m.

The results are listed in Table 8.

Table 8: Smoke Density Results in NBS Chamber (Smouldering Test Conditions)

Material	Treated with Comp. No.*	Values of** D_m	$t_{90\%}$	D_{90s}	SON	V_{max}	SOI
Fiber board	1	36.0	16.2	2.0	15.0	4.0	0.0877
Fiber board	1+10% Caliplast 613	48.2	15.8	2.9	30.0	6.8	0.390
Control	-	308	3.9	40	670	216	358

*Data with other compositions are quite similar to this.
**Lower value of D_m, D_{90s}, SoN, V_{max}, SOI, and higher value of $t_{90\%}$ better the performance of a material.

Table 9: Results of Scratch Hardness Test

Comp. No.	Maximum Load (gms) at Relative Humidities 40%	60%	80%	96%
1	2800	2750	2000	200
2	3000	2900	2100	270
3	3100	3100	2260	250
4	2700	2650	1900	175
5	2900	2800	1900	200
6	2850	2750	1950	200
7	2825	2800	1850	150

Scratch Hardness Test

The scratch hardness test apparatus consisted of a scratching needle with a hard ended steel hemispherical point of 1 mm diameter and a sliding panel to hold the specimen. The needle was fixed at the end of the counter poise, which was kept horizontal by adjusting the length of the needle at a rate of 30 to 40 mm per second. The tinned plate (150×50 mm, 0.315 m or 30 SWG) was coated with these paints.[14] The coated specimens were placed at 60°C for 24 hours and then allowed to cool. Different sets of assembled test specimens were conditioned at 40%, 60%, 80%, and 96% relative humidities for 48 hours. They were then subjected to scratch hardness test. The figures for different coatings, indicating the

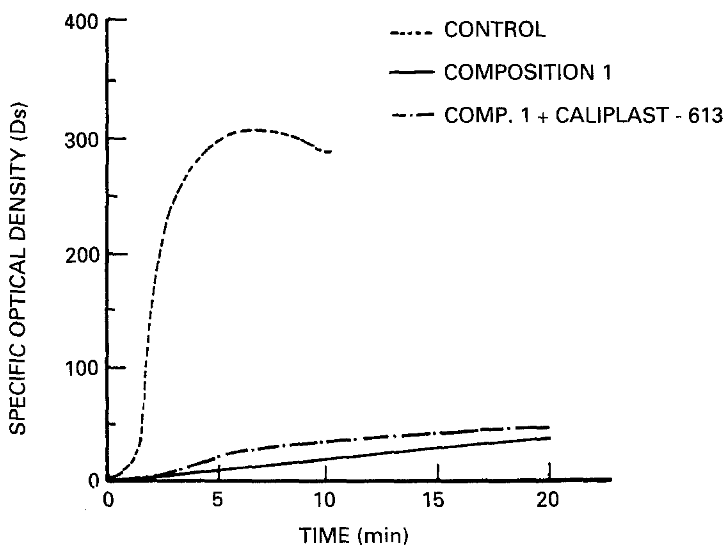

Figure 3: Effect of Coating on Smoke Generation.

Table 10: Results of Wet Resistance Test

Comp. No.	Additive	Weight of Ingredients on the Panel (gms)	Ingredients Leached Out from Panel (gms) After 1 hr.	5 hrs.	24 hrs.
1	-	31.485	11.140	21.335	23.732
1	Caliplast 613				
1	- 2%	31.495	8.821	9.462	11.012
1	- 4%	31.500	5.942	6.827	8.135
1	- 6%	31.504	3.261	4.020	5.146
1	- 8%	31.498	1.380	3.120	3.954
1	- 10%	31.500	1.272	2.016	2.785
1	- 12%	31.497	1.254	2.009	2.769
1	- 14%	31.495	1.249	2.012	2.754

maximum load applied to the needle allowing it to cut through the paint film up to the metal surface, are noted in Table 9.

Wet Resistance Test

As all the compositions of fire retardant paints studied contain water soluble salts, they are suitable only for indoor use in the absence of

Table 11: Fire Performance of Leached Specimen

Composition 1	Flame spread (sec.)	Afterglow (sec)	Weight Loss (gms)	Char Index (C.C)	Hght. of intum-escence (mm)
		After one hour leaching			
1(a)	4	22	6.25	14.94	8
3(b)	4	20	5.92	13.45	8
a+10% Caliplast 613(c)	0	0	2.95	1.80	11
b+10% Caliplast 613(d)	0	0	3.00	1.80	11
		After five hours leaching			
a	20	82	14.82	30.34	2
b	18	70	13.54	28.20	2
c	9	28	5.02	12.10	6
d	8	22	4.84	11.80	7
		After 24 hours leaching			
a	35	122	18.20	42.30	0
b	35	118	17.54	39.40	0
c	22	98	7.48	20.47	3
d	20	92	7.04	19.57	3

excessive humidity. In order to increase the water repellency of the coatings, a finishing coat of Caliplast 613 (VC/VA, copolymer) was applied. The specimens were subjected to continuous leaching under running water for one to 24 hours. The test samples were dried at 60°C for three days. The amount of fire retardant ingredients leached out was determined. The results with respect to leached out ingredients and fire performance of leached specimens are reported in Tables 10 and 11, respectively.

Moisture Absorption Test

The moisture absorption of the coatings on application of Caliplast 613 was determined after applying the paint on smooth and dried glass plates. The coated specimens were dried at 60°C for 72 hours followed by drying over calcium chloride. The specimens were then placed at 40%, 60%, 80%, and 96% controlled relative humidities for 48 hours. The moisture pick up by coatings is listed in Table 12.

Results and Discussions

When the main constituents of fire retardant intumescent coatings – i.e. amines, polyol, and ammonium phosphate (a catalyst) – are exposed to fire, the catalyst decomposes to produce phosphoric acid which acts as a dehydrating agent. The polyol is dehydrated by the acid forming a large amount of carbonaceous char that produces a noncombustible barrier to protect the substrate. The reactions, which take place on heating within the coating, may be expressed as:[7,15,16]

$$x(NH_4)_2HPO_4 \xrightarrow{\text{heat}} H-O\Big(\underset{\substack{|\\ O\\ H}}{\overset{\substack{|\\ O\\ |}}{P}}-O\Big)_x H + 2x\,NH_3 + (x-1)H_2O \qquad (1)$$

$$HO\Big(\underset{\substack{|\\ O\\ H}}{\overset{\substack{|\\ O\\ |}}{P}}\Big)H + R\,CH_2CH_2OH \rightarrow RCH_2CH_2OPO_3H_2 + HO\Big(\underset{\substack{|\\ OH}}{\overset{\substack{|\\ O\\ |}}{P}}-O\Big)_{x-1}H \qquad (2)$$

$$R\,CH_2CH_2OPO_3H_2 \underset{\text{heat}}{\overset{\text{more}}{\rightarrow}} RCH=CH_2 + H_3PO_4 \qquad (3)$$

$$xH_3PO_4 \xrightarrow{\text{heat}} HO\Big(\underset{\substack{|\\ O\\ H}}{\overset{\substack{|\\ O\\ |}}{P}}-O\Big)-H + (x-1)H_2O \qquad (4)$$

Table 12: Moisture Absorption by the Coatings

Comp. No.	Additive	Percent Moisture Pick Up at Relative Humidities 40%	60%	80%	96%
1 -		4.75	6.94	14.80	30.20
3 -		3.80	5.75	12.20	26.80
5 -		4.20	6.35	14.10	32.00
1	10% Caliplast-613	1.80	2.05	4.45	9.55
3	10% Caliplast-613	1.05	1.34	2.80	9.08
5	10% Caliplast-613	1.26	1.75	3.75	10.15

On heating, the binder softens and forms a covering over the surface of the carbonaceous char. This covering does not allow the gases produced by the blowing or spumific agents (amides) to escape. These spumific agents produce foamable carbon on giving off nonflammable gases providing effective insulation for protecting the material from heat.

The specimens, which were coated with the paint formulations under study, showed neither any surface spread of flame nor afterglow or smouldering on exposure. The combinations of polyol, dicyandiamide, and ammonium phosphate produced instant intumescence on exposure and showed minimum weight loss when used in the ration of 1:1.4:2.4 (Comp. 1), 1:1.5: 2.5 (Comp.2), and 1: 2: 2.5 (Comp. 3). Fire performance values remained the same on using either melamine or dicyandiamide. A satisfactory fire performance was achieved by replacing dicyandiamide or melamine by urea. The required ratio of polyol, urea, and ammonium phosphate was found to be 1:1.5:3.5 (Comp. 4). The paints containing Rollex 50, Calimul 6825, and Pidivyl C.P. 651 showed almost equal fire performance except that the height of intumescence in the case of Rollex 50 was lower (Comp. 5). When paint formulation with 5 percent Rollex 50 and 16 percent Calimul 6825 was used, the fire performance was decreased (Comp. 6). On using the formulation with less than 16 percent of Calimul 6825, better fire performance was achieved. However, the adhesion of the paint film was decreased (Comp. 7).

On applying the paint formulations on wood and plywood, fire performance was found to improve from Class 3 to Class 1. Similarly in the case of fiber board, it was found to improve from Class 4 to Class 1 (Tables 5 and 6). The index of performance as determined by BS 476 Part 6 test was significantly improved (Table 7). These formulations were also found quite effective in reducing the rate and the amount of smoke formed. The value of $t_{90\%}$ was increased from 3.9 minutes to 16.2 minutes indicating that the escape time was four times greater on using these paints. On using Caliplast 613, the amount of smoke increased from 36 to 48 Dm, whereas the value for control specimen was 308 Dm (Table 8).

The paint film resisted the effect of humidity up to 96% and did not detach itself from the surface thereby showing good adhesion. The ingredients of the paint films leached to a lesser extent under running water when cCaliplast 613 was used (Table 10). The moisture pick up by the paint film at higher humidities was also found to reduce when Caliplast 613 was used as a finishing coat (Table 12).

Conclusions

A few fire retardant intumescent coatings based on indigenously available chemicals have been developed that are found to be quite effective. The specimens with these coatings showed neither surface spread of flame nor afterglow combustion. On exposure, the paint film intumeses provided a spongy cellular insulating foam that acted as an effective barrier to the conduction of heat. Intumescent coatings developed are also suitable for absorbing lining materials such as fiber insulation board. The application of Caliplast 613 as a finishing coat increases the wet resistance of the coatings. Paints with binders Calimul 6825 and Pidivyl C.P. 651 are better in fire performance as well as in brush consistency. Although paints with Rollex 50 show better fire performance, their brush consistency is considerably reduced.

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References

1. Jain, J.P., et. al., "Fire Retardant Treatment for Absorbing Lining Materials," *The Fire Engineer*, **7** (July-Sept. 1982), pp. 9-15.
2. Baker, D.S., "Flame Retarding Wood and Timber Products," *Chemistry and Industry*, **2** (15 Jan. 1977), pp. 74-79.
3. Baker, D.S., "Wood in Fire, Flame Spread and Flame Retardant Treatments,"*Chemistry and Industry*, **14** (18 July 1981), pp. 485-490.
4. Jain, J.P., et. al., "Flame Spread in Wood and its Control," *Indian Planner & Builder*, **2**, *3* (1982), pp. 9-12.
5. Dua, A.C., "Fire Retardant Paints: Effect of Various Additives in Their Formulation," *Paint India*, **32**, *7* (1982), pp. 3-5.
6. Mishra, J.P. and Srivasamban, M.A., "Fire Retardant Coatings," *Paint India*, **29**, *6* (1979), pp. 21-26.
7. Lyons, J.W., "The Chemistry and Uses of Fire Retardants," *Wiley Intersciences*, New York (1970), pp. 248-272.
8. Bhatnagar, V.M. and Vergnaud, J.M., "Fire Retardant Paints," *Paint India*, **33**, *7* (1983), pp. 15-17.
9. Jain, J.P., et. al., "Fire Retardant Surface Coating for Cellulosic Materials,"

Research and Industry, **30** (1985), pp. 20-24.
10. ASTM D 1360, "Standard Method of Test for Fire Retardancy of Paints," (Cabinet Method), American Society for Testing and Materials, Philadelphia, PA 19103 (1979).
11. BS:476, "Fire Tests on Building Materials and Structures," Part 7, *Surface Spread of Flame Tests for Materials*, British Standard Institution, London (1971).
12. BS:476, "Fire Tests on Building Materials and Structures," Part 6, *Method of Test for Fire Propagation for Products*, British Standard Institution, London (1981).
13. ASTM E662, "Standard Test Method of Specific Optical Density of Smoke Generated by Solid Materials," American Society for Testing and Materials, Philadelphia, PA 19103 (1979).
14. IS:101, "Methods of Tests for Ready Mixed Paints and Enamels," Indian Standard Institution, Manak Bhavan 9, Bahadur Shah Zafar Marg, New Delhi 1 (1964).
15. Clark, F.B. and Lyons, J.W., "The Alcoholysis of Polyphosphoric Acid," *J. Amer. Chem. Soc.*, **88** (1966), pp. 4401-4405.
16. Smith, T., "Flame Resistant and Intumescent Paints and Compounds: A Review," *Pigment and Resin Technology,* **11**, *4* (1982), pp. 15-18; and **13**, *5* (1984), pp. 9-10.