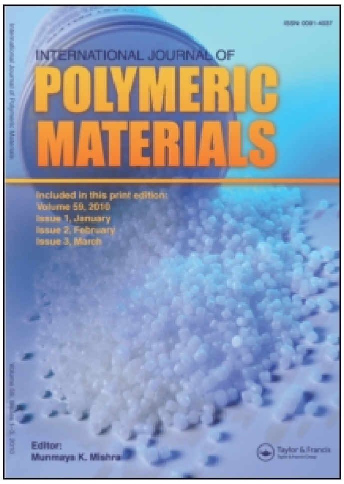

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Fire Retardant Decorative Laminates: Technology and Properties

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Fire resistance of High Pressure Decorative Laminates is investigated and the results reviewed in terms of fire resistance requirements.

KEY WORDS Laminates, formica, fire resistance.

INTRODUCTION

High Pressure Decorative Laminate (HPDL) is one of the most popular and widespread finishing materials used in furniture manufacturing, building construction and public transportation vehicles. Approximately 500 million sq. m (or approximately 750,000 t) of this material is produced in the world annually. HPDL is produced in almost all developed countries of the world and is known under the following trademarks: Formica, Nevermar, Pionite (USA); Perstorp (Sweden); Polyrey (France); Decola, Aica (Japan); Duropal, Resopal, Sprelacarte (Germany); Print (Italy); Melopan (Yugoslavia). There are more than 80 manufacturers all over the world.

HPDL is a composite material which consists of fillers of specially selected papers, impregnated with various polymers. (See Figure 1 and Table I.) Each layer has a separate function. Laminate composition and the number of layers vary considerably with different manufacturers. This article is based on the author's research at industrial amalgamation Mosstroyplastmass, Mytishi, USSR and covers the properties of HPDL flame retardant grades produced at the above-mentioned factory under the trademark "Manminit."

Tests on retardancy were performed according to methods used in the USSR on both standard and specially used materials in different industries. The Fire Tube (FT) test was performed on a 150 × 35 mm specimen. The specimen was subjected to the flame from a burner of a 40-mm high flame in a tube 165 mm long and 50 mm in diameter for 2 min. Test results are regarded as a pass if loss of weight does not exceed 20% and time of self-burning and smoldering is less than 60 sec.

The flame spread index I is a conventional value that shows the capability of

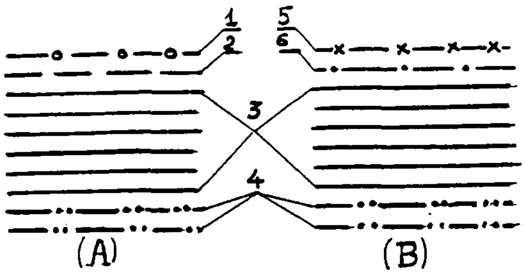

FIGURE 1 HPDL composition: (A) Multicolor HPDL; (B) Plain HPDL. (1) Overlay (protective) layer: overlay paper + melamine-formaldehyde polymer. (2) "Decorative layer: printed sheet + melamine-formaldehyde polymer. (3) Core: kraft paper + phenol-formaldehyde polymer. (5) Decorative layer. decorative unipaper + melamine-formaldehyde polymer. (6) Underlay (barrier sheet): barrier paper + melamine-formaldehyde polymer.

materials to spread flame across the surface as well as one that measures the maximum temperature of smoke gases, time to achieve the maximum temperature and the rate of flame spread across the surface of a 320 × 140 mm specimen subjected to heat flux 1.2 to 32 kW sq. m dense from radiant heat panel heated by a gas burner or an electrical spiral. Materials are classified as having a surface of slow flame spread when the index exceeds 20, and a surface of rapid flame spread when the index is above 20. This test is mainly used in the shipbuilding industry.

The burning index K is defined by a test performed on a 75 × 35 mm specimen burnt in a calorimeter. This index is the proportion of heat value discharged by a heated specimen to heat value coming from a source of ignition. Materials are classified as hard combustible when $0.1 \leq K \leq 0.5$; hard flammable when $0.5 \leq K \leq 2.1$; and combustible when $K \leq 2.1$.

The Limit of Burning (LB) is an oxygen index, where the specimen is subjected to the flame below.

Self-extinguishability (SE) is defined in a special furnace. A 290 × 70 mm specimen put in vertically is subjected to fire from a gas burner with a 40-mm high flame or from a spirit burner with a 20-mm high flame for 30 sec. After the burner is removed, self-burning and smoldering time should not exceed 15 sec. In such a case the material is regarded as self-extinguishable. If the time exceeds 15 sec., then the material is combustible. This method is used for testing aircraft materials.

If HPDL is used in public transportation vehicles (wall, ceiling, floor coverings and door claddings of carriages, trains and underground trains; ship furniture; finishing of sanitary rooms, restaurant tables on airplanes), then fire retardancy of the material (hereinafter referred to as HPDL Manminit) should be increased. According to Table I core layers of HPDL belong to hard flammable grades in accordance with burning index K, to the surface of rapid flame spread grade in accordance with index I (used in shipbuilding), as well as to combustible grade in accordance with value C (used in building aircraft).

Overlay (protective) and decorative layers are also of hard flammable grade, however, they are of slow surface flame spread grade and are self-extinguishable due to melamine retardant properties. Further reduction of combustibility of these layers seems rather difficult because fire retardants deteriorate the surface.

TABLE I

Composition and combustibility of HPDL and sample layers

Sample composition			Combustibility							
			FT		ZE					
Layer (sample)	Filler paper	Polymer, %	Weight loss, %	Burning, smouldering	Burning	Smouldering	Y	K	OI	LB
protective	overlay	MF, 70	12–16	none	none	none	1–3	0.5	42–45	30–33
barrier	underlay	MF40	14–18	none	none	none	4	–	38–42	26–28
decorative	printing	MF, 45	15–25	none	none	none	1–4	0.7–0.8	32–44	26–33
decorative	printing	MCF, 45	25–40	10–30	–	–	–	1.0–1.5	–	–
core	kraft	PhF, 30	60–75	>300	21	>60	18–40	1.9–2.1	32–38	22–26
core	kraft + NFR	PhF + MF30	12–20	2–18	2–4	none	4–6	–	48	25
core	kraft	PhF + DAPh, 35	15–20	3–25	2–5	none	4–10	0.8–1.1	–	–
HPDL	overlay	MF								
	printing	MF								
	kraft	PhF	50–70	>300	23	88	15–30	1.7–1.9	35–36	20–26
HPDL-M	overlay	MF								
	printing	MF								
	kraft	PhF + DAPh	14–20	6–18	2–5	none	8–12	0.7–1.0	–	–
HPDL-M	overlay	MF								
	printing	MF								
	kraft + NFR	PhF + MF	12–18	2–18	2–4	none	2–10	–	43–46	30–38

MF = melamine-formaldehyde; MCF = melamine-carbamide-formaldehyde; PhF = phenol-formaldehyde; DAPh = Diammonium Phosphate; NFR = nepheline fire retardant; HPDL–M = HPDL Manminit with slow flame spread across the surface.

Consequently, combustibility of core and balance layers, which make up 60–80% of HPDL weight and determine its fire retardancy, should be retarded.

REVIEW ON METHODS OF RETARDATION OF HPDL COMBUSTIBILITY

There are different methods of retarding combustibility of the HPDL core: addition of a chemically active fire retardant into phenol-formaldehyde oligomer during its synthesis; addition of a fire retardant into the treating compound; addition of fire retardant into paper pulp when paper is processed; prepregnated treating with a fire retardant; combination of different methods, defined above.

Quite a number of works have been devoted separately to combustibility and destruction of either phenol-formaldehyde and amino-formaldehyde polymers[1-6] or paper and cellulose.[7-9] However, combustibility of a laminate, which is a composition of phenol-formaldehyde and melamine-formaldehyde polymers and paper, where processes are interdependent and interconnected, is a separate problem.

The following treating compound was proposed: 35–50% phenol-formaldehyde polymer, 30–60% alcohol-water mixture, 1–10% alkylphosphates or their ammonium salts, 2–10% ammonium bromide.[10] In another case monoalcohol-aminophosphate, pentabromo-phenol and ammonium bromide were added to phenol resin.[11] Sweet and Hamill added 15–20% china clay to paper and then treated it with 20% monoammonium phosphate solution and further impregnated it with phenol-formaldehyde resin with added boric acid and sodium pentaborate.[12] In another case this paper was impregnated with a mixture of phenol-formaldehyde and melamine-formaldehyde resins in a proportion of 2:1 with orthoboric acid as a neutralizer and 5% sodium metaborate as an additive.[13] Phenol-formaldehyde resin may be added with secondary ammonium phosphate in combination with phosphoric acid, ammonia and free formaldehyde.[14] Phenol-formaldehyde resin may be added with phosphoric acid (phosphate 2% to 12%) and with different alcoholamines.[15]

Phosphoric, orthophosphoric or pyrophosphoric acid 1.5–3% of dry resin was added to bakelite varnish (alcohol solution of phenol-formaldehyde resin).[16] The same varnish was added with 3–12% phenol chlorine derivate, 1–5% tricresylphosphate, 3–10% urea.[17]

Zinc borate ($2ZnO \cdot B_2O_3 \cdot 2H_2O$) and small portions of antimony, tetrabromodiphenol, trichlorinepropylphosphate compounds were added to phenol-formaldehyde resin. This composition was used for impregnating paper containing up to 30% of asbestos fiber.[18] The paper was impregnated with phenol-formaldehyde composition, including oxides, hydroxides, phosphates, borates, silicates and carbonates of the following metals: magnesium, titanium, zinc, aluminium and antimony, as fire retardants.[19]

To retard combustibility, treating resin is frequently added with bromine compound, for instance, 3% of solid ammonium bromide[20]; or dibromophenyl monoglycidol ether with amines (benzyl dimethylamine, triethylenetetraamine, diamidodiphenyl sulfon, etc.)[21]; or alkyl aryl phosphate with organic compounds, where bromine is in the aromatic or aliphatic groups, or in both groups at the same time (e.g., pentabromodiphenyl ether and hexabromocyclododecane).[22] Pentabromodiphenyl ether with tribromo-, tetrabromo-, and hexabromodiphenyl ether additives were also used; average percentage of fire retardant is 5–15% of solid resin weight.[23]

Great Lakes, USA, produce a special grade of pentabromodiphenyl oxide under the trademark Great Lakes DE-71 used in water-based phenol-formaldehyde resins in 5–10% concentration.[24]

Halogen containing fire retardants are used either in combination with phosphorus[25] or antimony trioxide[26] compounds. Arylhaloalkyl phosphonate (e.g., cresyl-2-bromoethylmethyl phosphonate) is used in combination with chlorinated paraffins.[27] Phosphorus pentanitride is added into the treating compound in 4–15% concentration of solid resin.[28]

Various additives are used with paper pulp to reduce the combustibility of the laminate. For this purpose antimony trioxide and its synergistic effects with chlorine and nitrogen containing compounds are used.[29] It is advisable to add paper with antimony trioxide, chlorinated paraffin, PVC, polyvinylidene chloride, secondary ammonium phosphate, borax, tricresylphosphate.[30] A fire retardant, product of reaction of nefelin (aluminium silicate slag) and phosphoric acid and urea is also added to paper pulp.[31] It is possible to add paper with 5–30% red phosphorus or a mixture of red phosphorus with titanium dioxide, antimony trioxide and aluminium hydroxide.[32]

Paper is treated with orthophosphoric acid and neutralized with urea and dicyandiamide, up to 5–25% of dry fiber.[33] A 10%–18% mixture of ammonium sulfates with ammonium phosphates can be added to paper for impregnation.[34] Or it can be treated with phosphorus-modified organic sulphamates, produced under the trademark Albaplas; this product is easily combined with phenol-formaldehyde resins.[35]

To retard combustibility, dicyandiamide was added to the oligomer when synthesized in the following molar proportion: 1 phenol, 0.8–2 dicyandiamide, 1.5–3 formaldehyde.[36]

Some of the methods mentioned above were tested in the laboratory and found to be non-technological because organic solvents were used, or to be uneconomical because of the high cost of fire retardants. A detailed review of retardation of combustibility was submitted by Plotkin and Shalun.[37] Tests, performed in different countries, as well as classification of HPDL according to results obtained was defined by Probstain.[38]

TECHNOLOGY OF FIRE-RETARDANT DECORATIVE LAMINATE

Research carried out in the USSR and the USA proved that maximum fireproofness of phenol-formaldehyde polymers can be achieved by adding up to 6% phosphorus, and for cellulose up to 15% nitrogen or 3% phosphorus; it was also proved that using the synergism of the system of phosphorus plus nitrogen, the fire retardant content can be reduced. Since our matrix consists of phenol-formaldehyde polymer and cellulose, use of fire retardants containing nitrogen and phosphorus is most reasonable.[39]

The following determined the selection of the fire retardant: mass production in the USSR; competitive price; availability in the market; toxic safety; nonusage of organic solvents in the composition. Based on the conception above three matters were studied: diammonium phosphate (DAPh), nepheline fire retardant (NFR) and iron ammonium phosphate (IAPh).

The combustibility value of primary components cannot determine the combustibility of the laminate, although the combustibility value of prepreg is lower than that of filler; also the combustibility value of HPDL and sample layers is lower than that of prepreg. It is proved that a fire retardant performs its fire retardant properties mainly in finished products not in raw materials and semi-products. The oxygen index (OI) of overlay paper filler is 21, of prepreg consisting of the above-mentioned paper and melamine-formaldehyde oligomer is 32, sample laminate made of the above-mentioned prepreg is 37. The OI of decorative paper is 19, prepreg made of it and melamine formaldehyde oligomer is 31, sample laminate is 40. The OI of filler, fire retardant paper, is 18, of prepreg made of it and phenol-formaldehyde oligomer is 25, of sample laminate is 47. The OI of HPDL made of the three components above is 44.

Curves of thermogravimetric (TG) and differential thermal analysis (DTA) of prepregs of core paper, containing DAPh and NFR show that DAPh has a wider and more intense (DTA) exothermal peak—indicating burning, as well as a more intense (TG) peak corresponding to degradation. When we compare curves of HPDL, made of the prepregs defined above, the results are the opposite. Laminates based on the fire retardant nepheline have wider and more intensive peaks of DTA and DTG. Thus, it is proved that fire retardance shall be estimated by effect in a material, rather than in a filler or prepreg. Prepreg has noncuring resols (degree of curing 0–10%), which are of lower char-forming capacity in comparison with cured monolithic resins in HPDL. Content of inorganic filler in cellulose (up to 5%) physically affects the intensity of prepreg with NFR decomposition.

Combustibility of HPDL and the fire retardants mentioned above is most effectively reduced in the solid and not in the gas phase. Decomposition and combustion of decorative laminates is not a simple additive process; they are interdependent, as the three polymers (phenol-formaldehyde, melamine-formaldehyde and cellulose) and all the layers affect one other and change the values of separate components. Therefore combustibility was studied on laminates or samples of separate layers 1.0 mm, 1.6 mm, and 3.0 mm thick.

Technological data of the process are based on the machines and equipment operating at the Mosstroyplastmass factory without their reconstruction and expansion, as well as on the specific requirements of fire retardants defined above. Two technological processes of production of fire retardant laminates are developed: the first is based on diammonium phosphate, added to the phenol-formaldehyde oligomer; the second is based on the fire retardant nepheline, added to the filler, paper.

The curves in Figure 2 show that the optimum quantity of DAPh added to the phenol-formaldehyde oligomer is 4–6% of the total mass of prepreg (or 3–4% of the total mass of HPDL-M, or 11–13% of the total mass of the phenol-formaldehyde oligomer). It is equal to 2.5% P + 2.5% N in oligomer (or 1% P + 1%

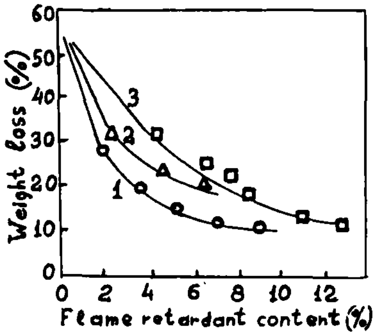

FIGURE 2 Curves of weight loss (fire tube) of core layer sample with fire retardant: (1) DAPh in phenol-formaldehyde oligomer; (2) DAPh in paper; (3) NFR in paper.

N in prepreg). A further increase in the DAPh percentage slightly retards combustibility, however, it lowers strength and water absorption values, moreover, the treating speed becomes rather low and economically unreasonable. Synthesis of the phenol-formaldehyde oligomer is performed at parameters similar to those of oligomer synthesis for standard HPDL. DAPh is dissolved in water and mixed with the phenol-formaldehyde oligomer. The finished composition is used in the treating process (see the parameters in Table II).

Nepheline fire retardant, containing 46–50% P_2O_5 and 3–5% NH_3, is added to paper during the production process, in quantities of 10–14% of its total mass. The value above is determined by the essential requirements of combustibility, such as weight loss (Figure 2) and self-burning smoldering times (Figure 3). Thus, the physical and mechanical data of both filler and laminate are preserved. Up to 1% melamine-formaldehyde resin is added to the paper to improve its wet tensile strength. Due to fire retardance the filler has 2.8% P and 0.25% N, and due to wet tensile strength additive it has 0.45% N; the total proportion P:N is 4.6:1. Finished fire retardant high wet tensile strength paper of 160 + 5 g/m^2, 280–310 mkm thick, has wet tensile strength in machine direction of 88 Newton. This product provides the required technical characteristics for HPDL-M. To achieve optimum nitrogen percentage (from the point of view of the synergistic effect), an additional quantity of nitrogen is added to the phenol-formaldehyde oligomer by adding 2–3% of the melamine-formaldehyde oligomer before the treating process. In such a way the proportion of P:N in prepreg is raised to 2:1 (~1.8% and ~0.9%). The elaborated technology (see the parameters in Table II) provided a rise in productivity of the treating process by 200–300%.[40]

The main role in inhibiting HPDL combustion is played by char, by laminated carbonized layer in particular, which reduces the speed of emission of degradation products to the gas phase; reduces heat, absorbed by the polymer, as the consumption of thermal energy is reduced by convection and heat discharge is increased by radiation due to the rise in temperature of the char surface; makes a barrier for heat flow from flame, expands the delay time of ignition. The combination of phosphorus and nitrogen causes dehydration of cellulose and of phenol-formaldehyde polymer and an increase in emission of carbonized residue and a reduction of char penetration.

TABLE II

Technology of fillers impregnation in HPDL-M production

	Process (fire retardant)	
Description	Diammonium phosphate	Nepheline
I. Impregnation compound		
Binder, %	37–42	48–55
Fire retardant, dry mass to dry basis, %	12	-
Water, %	58–63	45–52
Viscosity, mPa	12–25	35–70
II. Filler		
Paper composition, %:.		
Cellulose	100	85–90
Fire retardant	–	10–15
Weight 1 sq. m, g	160 + 5	160 + 5
III. Prepregnation		
Composition, %:		
Cellulose	60–66	61–63
Phenol-formaldehyde oligomer	30–35.5	28–29
Melamine-formaldehyde oligomer	–	2–1
Fire-retardant:		
Diammonium phosphate	4–4.5	
Nepheline	–	6–9
Weight 1 sq. m, g	246–266	228–246
IV. Technological data		
Paper impregnation rate, m/min	35–45	90–100
Water, evaporated for 1 sq. m prepreg production, g	109	64
Quantity of heat for 1 sq. m prepreg production, kJ (kcal)	282(67)	168(40)
Heat consumption in the dryer for 1 sq. m of laminate production kJ (kcal)	2310(551)	1386(330)
Temperature, °C	100–170	100–170
V. Consumption		
HPDL g/sq. m:		
Paper	1500	1513
Oligomers	966	891

A rise in the fire retardant percentage increases char residue (CR) up to a certain maximum, which is 46–48% for DAPh and 38–41% for NFR (Figure 4). Further rise in the percentage of fire retardant does not increase the CR. DAPh is more effective from the point of view of carbonized layer formation, as it achieves maximum at 3–5% in prepreg, although NFR achieves maximum at 6–7%.

Methods of spectral emission analysis (blackening of the phosphorus spectral line in spectra of laminate and char residue samples) as well as methods of quantitative elementary analysis show that char P, N and carbon are enriched; their percentage increases by 1.5–2 in comparison with the primary laminate, and at the same time oxygen and hydrogen are reduced. See Table III.

Comparing Figures 2 and 3 and consequent results, taking into account the fact that with Iron Ammonium Phosphate HPDL-M 1.6-mm thick cannot be produced to meet the requirements of transport vehicles, efficiency of the fire retardants in question can be shown in the following sequence: DAPh (23% P + 21% N) >

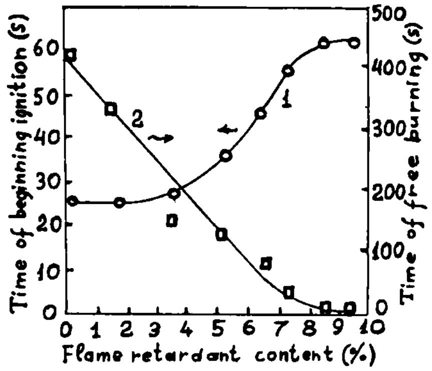

FIGURE 3 Time changes of: (1) free burning and smoldering—T1 and (2) beginning of ignition—T2. (Fire retardant—NFR.)

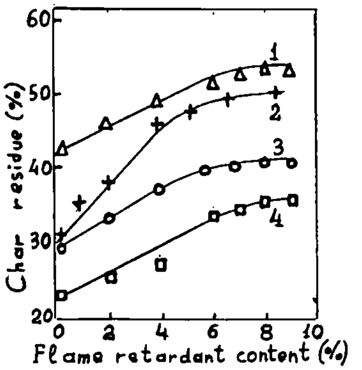

FIGURE 4 Curves of char residue for core layer sample: (1, 2, 3) NFR; (4) DAPh; (1) 400°C; (2, 4) 600°C; (3) 850°C. (T = 10 min.)

TABLE III

Elementary composition of samples and their char

Elements, % of total mass	P	N	C	H	O	Me, Si
Core layer sample with DAPh	1.3	0.7	48	6	44	
Char of core layer sample with DAPh	2	1.5	84	3	9.5	
Core layer sample with NFR	1.3	0.3	48	5.6	41.8	3
Char of core layer with NFR	2.6	0.6	67	3	20.8	6
Protective layer sample		32	36.8	5.2	26	
Char of protective layer sample		32.4	53	2.6	12	

NFR (22% P + 4% N) > IAPh (14% P + 4% N). DAPh is also more acceptable from a synergistic point of view, where the proportion of P:N = 1:1, which (according to sources in the literature) is optimal and is proved by experiment.

Thermal degradation of HPDL, HPDL-M, and of core layer samples with DAPh and without it (Figure 5) show that in the presence of diammonium phosphate at the initial stage of decomposition, the volume of escaped matter is larger than that of the samples, which do not contain fire retardants. At from 310–330°C the

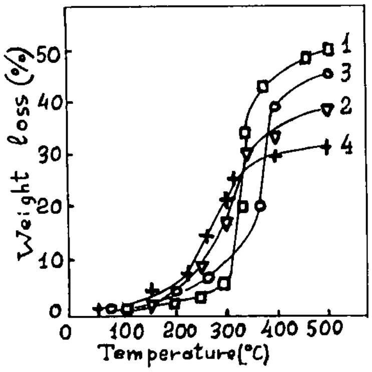

FIGURE 5 Loss of weight when heated in vacuum: (1) HPDL; (2) HPDL-M (DAPh 2%); (3, 4) core layer sample. (4–5% DAPh.)

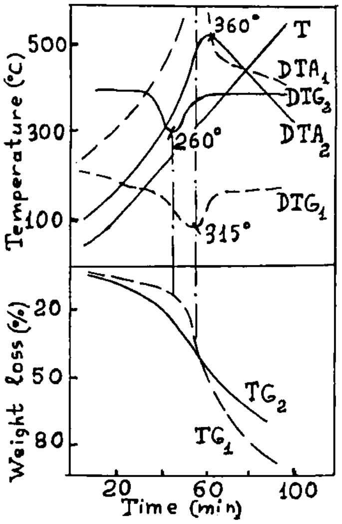

FIGURE 6 Curves of thermogravimetric (TG, DTG) and differential thermal analysis (DTA) of core layer sample for: (1) HPDL; (2) for HPDL-M with 6.5% DAPh.

emission of this matter reduces and becomes less than that of standard laminates. Further heating shows considerable difference in favor of the fire retarded material, due to the formation of char and a slower rate of emission of volatile matters by degradation. The difference between core layer samples is larger than between HPDL and HPDL-M due to additional char formation of the decorative layer.[41]

Differential thermal and thermogravimetric analysis of the same samples show (Figure 6) that the core layer sample has a maximum rate of decomposition at 315°C and at the same temperature it has intensive burning and DTA peak. Two phenomena were discovered in the presence of fire retardant. First, the weight loss of degradation products is reduced within the limits of the maximum rate of decomposition; moreover, the limits are kept in the zone of lower temperatures from 315°C to 260–270°C. Second, burning continues at higher temperatures at 360°C and DTA peak intensity within these limits is not high, thus proving the extinguishing capability of the fire retardant.

PROPERTIES OF REDUCED COMBUSTIBILITY OF HPDL-M

The provided material is used in the finishing of different surfaces: ceilings, walls, cabin compartments and corridors of ships; and carriages; furniture on ships; door claddings; interior surfaces of apartments and furniture of sanitary rooms in airplanes; ceilings, walls and doors of elevators; doors, built-in furniture and wall panels in civil construction. HPDL-M in combination with other polymer materials make transport vehicles fire hazardous. The approximate levels of impregnation of laminate made for various applications are: for underground carriages 1.5 $\mathrm{kg \cdot m^{-3}}$; for carriages of a country train 1.25 $\mathrm{kg \cdot m^{-3}}$; passenger carriages 4 $\mathrm{kg \cdot m^{-3}}$; for cabins 3 $\mathrm{kg \cdot m^{-3}}$; passenger elevators 9 $\mathrm{kg \cdot m^{-3}}$.

Since large surfaces of premices and evacuation corridors are covered with HPDL-M, it has become necessary to check performance characteristics not only according to different standards, but on larger samples, similar to real applications, in normal situations including burning.

Standard methods measure combustibility without varying the supply of oxidizing medium. However, because of layer after layer burning and char formation the burning rate changes continuously and in fire situation air excess varies from 3 to 5. Therefore research was carried out with special equipment with continuous measuring of sample weight, constant supply of air and variation of coefficient of excess air, L, from 1 to 3.

It is determined that HPDL with DAPh and for the sample of core layer with DAPh maximum mass burning rate, G max, slightly depends on L and amounts to 10–25 $\mathrm{g \cdot min^{-1}}$ (Figure 7). For standard laminate and a sample G max is 120–130 $\mathrm{g \cdot m^{-1}}$ at $L = 2$, and at $L = 1$ and at $L = 3$ from 70 to 80 $\mathrm{g \cdot min^{-1}}$.

The mass burning rate for non-fire-retardant HPDL and a sample of its core layer at $L = 2$ maximum is achieved within 3–4 minutes, and at $L = 1$ and $L = 3$ G max is achieved within 6–9 minutes correspondingly. For HPDL-M with DAPh

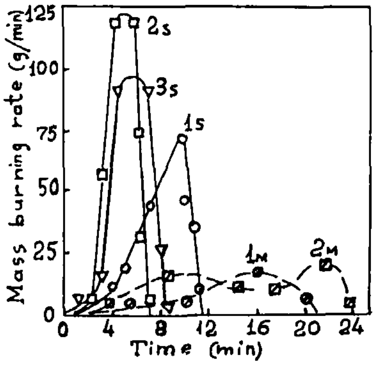

FIGURE 7 Mass burning rate in the furnace. H-HPDL; M-HPDL-M; (1, 2, 3) coefficient of excess air.

and a sample of its core layer *G* max is achieved within 10–20 minutes, and complete burning is achieved within 15–24 minutes; moreover, for HPDL-M the worst conditions are at $L = 3$, and for core layer sample it does not depend on *L*.

The maximum average gas temperature in the oven depending on excess of air for HPDL with DAPh is 250–380°C, and for the sample of its core layer it is 450–510°C. The corresponding temperatures in the smoke tube is 100–140°C and 190–200°C (Figure 8). Standard HPDL has temperatures of 690–760°C and in the smoke tube 500–570°C, core layer sample temperature is 620–650°C and 420–550°C correspondingly, which is close to temperatures reached at testing of pinewood board. Maximum average gas temperature in the oven and in the smoke tube depend on air excess slightly, as well as type of material. However, the time it takes to achieve maximum temperature depends on *L* and is from 2–8 minutes for non-fire-retarded materials and from 8–14 minutes for fire-retarded materials.

HPDL-M as an independent construction material is used only for the finishing of vertical surfaces in underground carriages and elevators; in all other cases it is bonded to a substrate. Therefore, flame spread indexes, *J*, are measured for HPDL-M in composition with various substrates, which proves that although the flame spread index is reduced, necessary results cannot be achieved if the substrate material is highly fire hazardous (Table IV).

HPDL combustibility was measured not only by standard and laboratory tests performed on small specimens, as described above, but it was also evaluated on special equipment, where parameters and dimensions were similar to the practical situation of ignition and flame spread.

Wide-scale experimental tests performed in the "Tunnel Furnace" showed that flame spread beyond the jet zone of HPDL subjected to Local Ignition Source (LIS) (with jet temperature 1000°C and section 0.15 sq. m); at average gas temperature 150°C auto-ignition of HPDL subjected to Radiative Heat Flux (RHF) occurred with further flame spread across the surface and complete burning up of the material (Figure 9). In the jet zone of HPDL-M subjected to LIS, the material becomes charred and flame does not spread. At average gas temperature 200°C

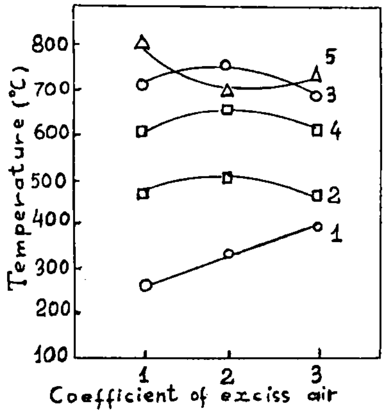

FIGURE 8 Temperature in air furnace: (1) HPDL-M (DAPh); (2) core layer sample (DAPh); (3) HPDL; (4) core layer sample; (5) pinewood substrate.

TABLE IV

Test of HPDL-M in composition

Material description	Thickness (mm)	J	
		Composition	Material
Asbestos cement board	25	7.5	0
Particle board	20	24.5	70
Joiner's board	20	25	80
Polyurethane foam	16	16.5	28
Plywood	10	25	80
HPDL-M	1.6	–	11.5

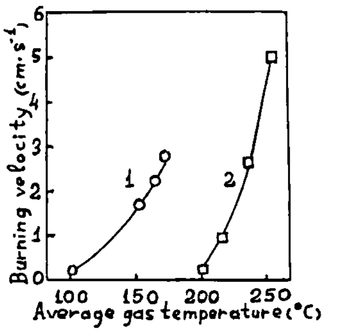

FIGURE 9 Test in the tunnel furnace: (1) HPDL; (2) HPDL-M. (3.6% DAPh.)

auto-ignition of HPDL-M subjected to RHF occurs and flame spreads across the surface. Thus, the critical temperature (exceeding this limit causes spread of flame beyond the LIS zone), with reserve coefficient 0.8, for HPDL is 80°C, for HPDL-M it is 160°C, and for HPDL-M bonded to asbestos cement board it is 180°C. HPDL belongs to flame spread class 4, and the other two samples belong to class 3. Under conditions of a fire situation, addition of DAPh increases critical temperature by 2 and reduces the flame spread class.

Ignition capability determines the possibility of ignition from small-scale sources, because in real situations they are the main sources of fire (a nonextinguished cigarette, match, paper, etc.). Measuring of ignition temperature by low-calorie current source—T3 (minimum temperature Ni-Cr alloy wire 40-mm long and 2.5-mm in diameter, giving heat flux 10 $W \cdot cm^{-2}$ and pressed to surface under test) shows the following dependence in the row filler → prepreg → laminate for T3: overlay 950°C → 1055°C → 1105°C; decorative layer 1045°C → 1085°C 1105°C; core layer 1025°C → 1072°C → 1110°C; core layer with NFR 1037°C → 1078°C → 1093°C; HPDL 1093°C; HPDL-M 1100°C. Ignition temperature of fillers (excluding overlay) are similar and are about 30°C; T3 of prepregs are about 30°C; T3 of layers and laminate sample are about 20°C. Thus, ignition is caused by a flash in the gas phase of products of degradation of the material caused by heat flux. However, further ignition stops (or slows down) due to fire retardance. In the same test, but performed in the medium enriched with oxygen up to 50%, the flame spread rate for HPDL-M is 1.4 times less than for HPDL; and for the core sample with nepheline fire retardant it is 2.5 times less than without fire retardant.

Ignition, rise of fire and burning velocity (BV) across the surface depend considerably on the external rate of heat flow, q. Therefore, BV and the critical heat flux q were studied within the range of heat flux 11–34 $kW \cdot m^{-2}$ by special equipment (ISO project 5658, size of specimen 800 × 140 mm). For HPDL in positions "wall" and "floor" q is correspondingly 15, 7 and 22 $kW \cdot m^{-2}$, for core layer samples 12 and 20 $kW \cdot m^{-2}$; for HPDL-M (with nepheline fire retardant) q is correspondingly 19.2 and 32 $kW \cdot m^{-2}$, and for its core layer sample it is 22.1 and 25 $kW \cdot m^{-2}$.

BV across the HPDL surface and sample of its core layer is considerably higher than that of HPDL-M and the sample with fire retardant.

For position "wall" the above can be seen in Figure 10. For position "floor" with equal heat fluxes, burning velocity is either very low or is zero. Even if the heat flux is increased by 40–50%, the burning velocity is considerably lower than in position "wall."[42]

When ignition is studied in the "Fire Box," maximum variation of temperature of emission gas from that of standard for HPDL without fire retardant is 2.5 times greater, time of reaching maximum temperature is 10% less, and the rate of temperature increase is 2.5 times greater than for HPDL with fire retardant (Figure 11).

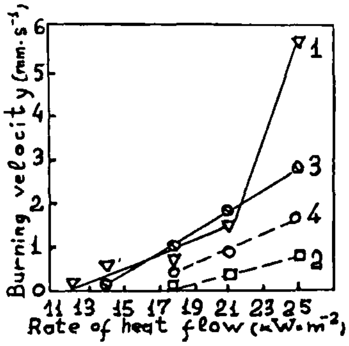

FIGURE 10 Rate of heat flow: (1) core layer sample; (2) the same with NFR; (3) HPDL; (4) HPDL-M with NFR.

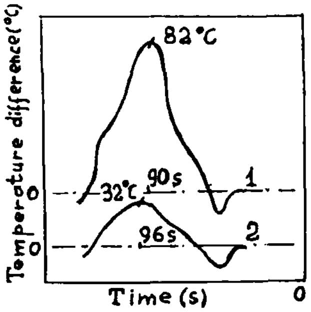

FIGURE 11 Test in the fire box: (1) HPDL; (2) HPDL-M.

CONCLUSION

The developed and manufactured in mass production HPDL conforms to standard laminate and its general characteristics comply with international standard ISO 4586, class S. Moreover, it complies with fireproof requirements, existing in the USSR, which determine the possibility of its specific application in public and military machinery, in polar and tropical conditions, long-term stability of physical and mechanical and aesthetic values against exposure to various exterior effects. The data received in the laboratory are confirmed with tests of trial lots, as well as a summary of results of operation of all kinds of vessels in different climatic conditions within 20 years.

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