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Special Review

STUDY OF THE COMBUSTION OF A FIRE RETARDANT COATING BY THERMAL ANALYSIS AND DIFFERENT COMPLEMENTARY TECHNIQUES

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An intumescent fire retardant coating can effectively control fire spread and damage. Its dual purpose is to confine the surface spread of flame to the boundaries of an already established fire, and to retard the penetration of heat and flame to and through the coated surface. Our composition expanded and provided an insulation layer between the flame source and the combustion substrate, and liberated a quantity of primarily non-flammable decomposition products which tended to extinguish the flame. The main ingredients of the coating were cellulose acetate butyrate and HMDI (Desmodur N) for polyurethane, and Chlorowax-70 (chlorinated paraffins) as fire retardant component. This fire retardant coating was applied to wood panels, and tested in a 2-foot tunnel, its flame spread rating being measured. The effects of three parameters of interest were investigated: the type of wood used, the percentage of Chlorowax, and the coating thickness. It was found of interest to study the oxidation of the coating using different techniques, e.g. flash pyrolysis under oxygen and GC/MS for analysis of the decomposed products. Combustion studies of the coating were also conducted using DSC and thermogravimetry, either with the scanning mode or under isothermal conditions. Comparisons were made between the results obtained from pyrolysis and combustion.

When wood is exposed to external heating, it undergoes thermal degradation giving off flammable or combustible gases and leaving behind a charcoal residue. Flaming takes place if the rate of emission of these gases or volatiles is sufficient to form a combustible mixture with the surrounding air. Ignition of wood usually occurs at surface temperatures of 300 to 430° depending on the type of wood and the distance of the ignition source from wood surface.

An intumescent fire retardant coating can effectively control fire spread and provide sufficient time for the evacuation of personnel. Its dual purpose is to confine

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the surface spread of flame to the boundary of the already established fire, and to retard penetration of heat and flame to, and through, the coated surface. The scheme showing the behaviour of a fire retardant coating when exposed to fire, is given in Fig. 1. Two transfers take place from the fire to the surface of the coating: a heat transfer responsible for the heating of the coating and the wood, and a mass transfer responsible for the combustion when associated with oxygen. Decomposition of the coating, or rather part of it, takes place with a low endothermic effect and non-flammable gases are given off. These gases hinder oxygen diffusion and transfer to the coating surface and reduce the exothermic reaction of the combustion. Another interesting phenomenon takes place with an intumescent fire retardant coating: when the end of pyrolysis is drawing near, a swollen crust remains on the solid material surface, with a low heat transfer conductivity. This puffed up or intumesced crust is not flammable and provides further protection of the wood against the fire. Of course, the coating is not sufficient to withstand a large fire. However both these effects (non-flammable gas production and the low heat transfer of crust) retard the propagation of the fire, and this delayed fire effect is of great interest in fire technology.

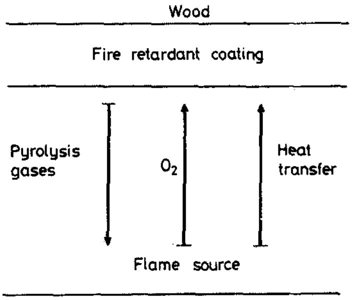

Fig. 1 Scheme of a substrate and fire retardant coating exposed to the flame

Thus the main object of this work is to study a clear fire retardant coating having application characteristics of a high quality coating. The main ingredients of the composition are: cellulose acetate butyrate and Desmodur N for PU, and Chlorowax-70 a chlorinated paraffin as the fire retardant [1, 2]. This composition was found [3] to expand and provide an insulation layer between the flame source and the combustion substrate. On decomposition, the coating liberated a quantity of non-flammable products which tended to extinguish the flame or slow its advance.

The coating applied to wood panels was tested in a 2-foot tunnel. The flame spread rating was measured and the effect of 3 parameters of interest i.e. the type of wood, the percentage of Chlorowax, and the coating thickness were investigated.

DSC and thermogravimetry experiments were performed either with the scanning mode or under isothermal conditions. The coating was also subjected to oxidation using flash pyrolysis under oxygen, and the decomposition products were analysed by GC/MS.

Experimental

1. Preparation of fire retardant coating [3, 4]

The main ingredients of the coating were cellulose acetate butyrate and HMDI for the PU, Chlorowax-70 (Diamond–Shamrock Chemical) as chlorinated paraffin, and methyl isobutyl ketone as solvent. Desmodur N was used instead of HMDI in this work; it resulted from the reduction of 3 moles of HMDI with 1 mole of water and the release of 1 mole of CO_2. Cellulose acetate butyrate is a resin suitable for coating purposes. Dibutylin dilaurate and Desmorapid were added to improve the drying slip properties of the coating. The chlorinated hydrocarbon and cellulose acetate butyrate were blended together in the solvent as component A, and the polyisocyanate was added as component B.

Component A	Cellulose acetate butyrate	48
	Chlorinated paraffin	18
	Mar and slip additive	0.6
Component B	Desmodur N	33.4

The coating dried tack-free within 1 hour or less, and required about 2 days to reach maximum hardness.

2. Fire retardancy test

A 2-foot tunnel [5] was used to test the coated panels. The sample holding rack utilizes a 30 in. by 4 in. specimen and is inclined at 30° to the horizontal. The coating was subjected to the flame for 4 minutes. During this time, the length of the flame front as it spread along the surface was recorded every 20 s. The flame spread rating, FSR, was calculated from the maximum front advance on the panel surface as compared with that of red-oak and asbestos millboard, which are arbitrarily assigned values of 100 and 0, respectively:

$$\mathrm{FSR} = 100\,\frac{L_{\mathrm{sample}} - L_{\mathrm{asbestos}}}{L_{\mathrm{oak}} - L_{\mathrm{asbestos}}}$$

where L was the average maximum length of the flame front on the chosen material.

3. Thermogravimetry

TG studies were conducted using an Ugine–Eyraud G 70 (Setaram) thermobalance under isothermal conditions. Measurements were carried out in air. The sample weighed about 200 mg. The loss in weight was recorded continuously.

4. Calorimeter

A DSC 111 (Setaram) differential scanning calorimeter was used. About 10 mg of sample was deposited on the aluminium holder. Measurements were made in the presence of air.

5. *Flash pyrolysis system*

For this study, the coating samples were employed in different ways: scraping of a dried coating layer deposited on a glass surface, or soaking the pyrolysis wire with the coating solution and evaporating the solvent. In both cases, about 0.5 mg of the sample was inserted into the pyrolyzer.

A CDS Pyroprobe was coupled to a Varian 3700 GC and a Varian 1440–Mat 112 spectrophotometer. The experiment was carried out at 400, 600 or 800°. The temperature of the pyrolysis chamber was 94°. The rate of heating was about 10.000 deg/s for the wire, with a pyrolysis time of 10 s. The amount of air circulated in the pyrolysis chamber was more than needed for the oxidation.

The GC was equipped with a 50 cm Tenax precolumn and a 150 cm column containing 3% SE 30 supported on a carrier. In other experiments, a 5 cm zeolite precolumn followed by a 150 cm Porapak Q column was used. The carrier gas was helium (16 cm^3/min). The temperature conditions were 230° for the injector and 320° for the detector. The temperature programme of the column was started at 60° and than raised gradually, at 20 deg/min, up to 300°.

Results

1. *Fire retardancy measurements*

The effects of three parameters were investigated: the type of wood used, the percentage of Chlorowax-70, and the coating thickness.

– *Effect of type of wood*

Our coating formulation was tested on several types of wood, using a dry film thickness of 0.24 mm (10 mils) as shown in Table 1. The relative decrease in the FSR was roughly the same for the different kinds of woods.

Table 1 Dependence of the FSR on the kind of wood

Wood	Uncoated	Coated	Relative decrease
Poplar	128	65	0.53
Red oak	100	50	0.50
Douglas fir	115	45	0.61
Birch	110	43	0.59
Masonite	90	41	0.54
Asbestos	0	—	—

– *Effect of Chlorowax-70 content*

Results are illustrated in Fig. 2, which shows the FSR against the proportion by weight of Chlorowax-70, in the range 0–40%. While it might appear logical that in-

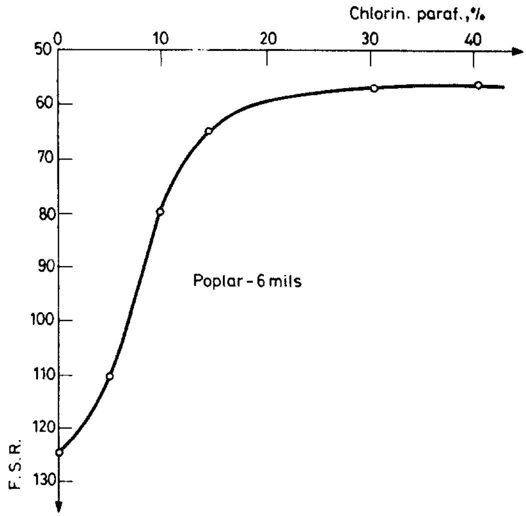

Fig. 2 FSR as a function of % Chlorowax-70. Poplar. 6 mils for coating thickness

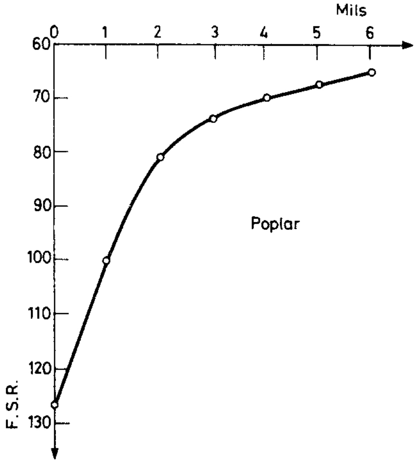

Fig. 3 FSR as a function of coating thickness (mil). Poplar. 20% Chlorowax-70

creasing the amount of Chlorowax-70 will provide more insulation or foam thickness, Fig. 4 shows that this is not always the case. Beyond a value of 17%, increase in the Chlorowax-70 content did not decrease or affect the FSR to any appreciable extent.

– *Effect of coating thickness*

Figure 3 shows a significant increase in flame retardancy properties with increase in the number of coats. The optimum film thickness was 5–6 mils; beyond this, any increase in thickness had only a relatively small effect on the FSR. Attempts were made to develop a first-order equation covering all the values. Table 2 gives the ratio of the relative decrease in the FSR to the coating thickness. In principle, our experimental values agreed with the equation, but the accuracy was not so good as desired.

Table 2 Variation of K with coating thickness

Thickness (mil)	1	2	3	4	5	6
K	0.25	0.22	0.18	0.16	0.14	0.12

$$\frac{d[\mathrm{FSR}]}{\mathrm{FSR}} = K \cdot [\text{coating thickness}]$$

2. *TG studies*

– *TG results under dynamic conditions*

Typical curves are given in Fig. 4 for the PU and the coating (PU + Chlorowax) with heating at 4.5 deg $\min^{-1}$ in air. Comparison of these curves with curves obtained under the same conditions but in an inert gas or in vacuum revealed that the degradation actually took place in two different steps, depending on the temperature of pyrolysis. For temperatures below 350–400°, the degradation was controlled by pyrolysis and the curves obtained in air were almost the same as those determined in nitrogen or in vacuum. The behaviours of the PU and the coating were quite different since the loss in weight started at about 150° for the coating and at 200° for the PU alone. This result could be explained by the higher volatility or decomposition rate of Chlorowax. Throughout the loss in weight range 5–55%, the curves were

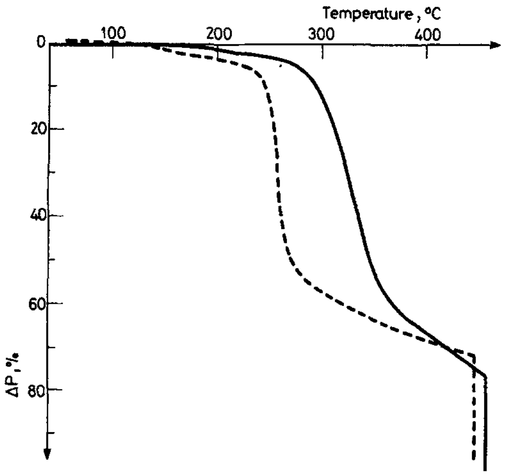

Fig. 4 Thermal curves of the PU and the coating in air with a heating rate of 4.5 °C/min

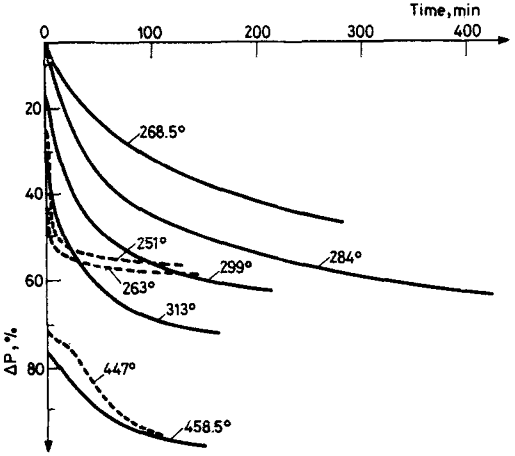

Fig. 5 Isothermal TG of the PU and the coating in air

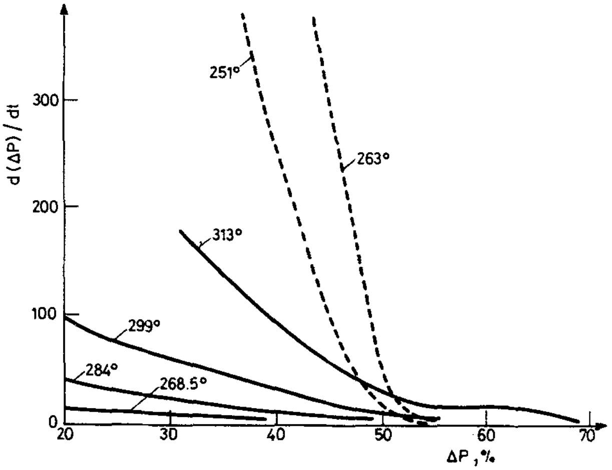

Fig. 6 Pyrolysis rate as a function of weight loss of PU and coating, for kinetic treatment

almost parallel, but for a higher weight loss (around 65%) at 400° these curves intersected.

At temperatures around 450°, a different process controlled the degradation, since combustion took place for both PU and coating samples. The rate of weight loss was particularly fast in this stage. This was the main observed difference between the curves studied in nitrogen and in air.

– TG results under isothermal conditions

Figure 5 compares the isothermal degradation in air of the PU alone and the coating at different temperatures. For temperatures below 400°, at the start of degradation for a time less than 10 minutes, the rate of weight loss for the coating was higher than for the PU alone. All these isothermal curves displayed an asymptotic tendency at high degradation times. Asymptotic values were lower for the coating (60%) and higher for the PU alone (80%). For temperatures around 450° and higher, the rate of degradation was very fast for both the PU and the coating as the reaction was near completion. This decomposition in air therefore differed considerably from the pyrolysis in nitrogen.

Kinetic studies were carried out on the decomposition of the coating and the PU by plotting the rate of decomposition against the loss in weight, as shown in Fig. 6. The overall degradation was found to obey a first-order reaction.

3. DSC studies

The behaviour of the PU alone and the coating in air is shown in Fig. 7, where DSC was programmed from room temperature up to 500° at a rate of 10 deg/min. These curves were quite different. The coating showed a peak at around 270° and a

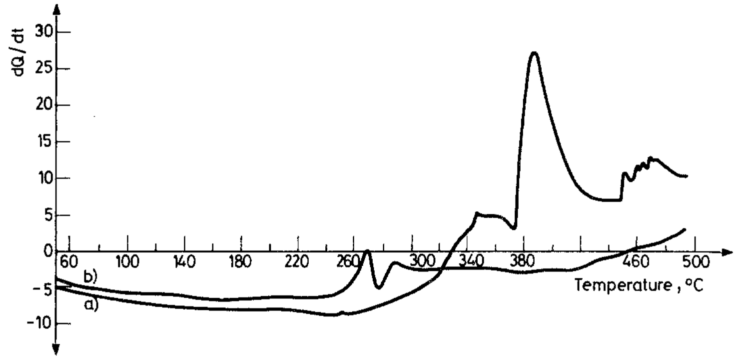

Fig. 7 DSC of the PU and the coating in air. (a) PU, weight: 8.57 mg, $dT/dt = 10$ deg/min, atmosphere: air; (b) PU + Chlorowax: weight 8.41 mg

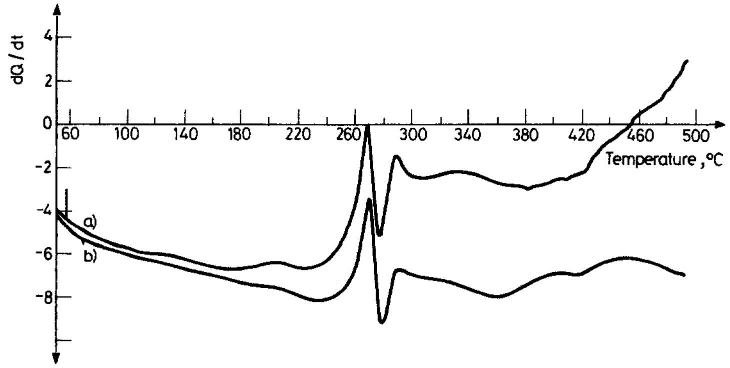

Fig. 8 DSC of the coating in air and argon. PU + Chlorowax, weight: 8.41, $dT/dt = 10$ deg/min, (a) in air; (b) in argon weight: 8.99 mg

slight thermal effect above 430°. The PU alone showed a very large peak at around 380°, located between two smaller peaks at 350 and 450°. A comparison is made in Fig. 8 between DSC curves obtained in air and in argon for the coating. A peak at 270° is observed in both curves. However, a difference between these curves appears at 430°.

Two conclusions were derived from these qualitative data: the PU alone began to ignite or burn quickly at 380°; the coating did not burn as soon as the PU did and the ignition temperature was higher, at around 420°.

4. Flash pyrolysis studies

The combustion products of Chlorowax-70 at 600° are shown in Table 3, while those of the coating are given in Table 4.

The study showed that for the Chlorowax-70, only a part of the degradation was achieved at 400°. The same decomposition products were formed at 400 and 600°, except that for at 600° nitrogen derivatives as acrylonitrile and imidazole were also found (Table 5).

Another complementary analysis was carried out on the degradation products at 400 and 600°. Several oxygen-bearing compounds such as ketone, acetic acid, etc, . . . were observed (Table 6). It was also clearly evident that the coating began to degrade at 400°, but it evolved combustion products at 600° with a large amount of CO_2 at a more rapid rate.

Table 3 Combustion products of Chlorowax at 600°

CO_2
Chloroethylene + chloroethane
Chloroethane + HCl + dichloroethylene
Chloroethane
Chlorobenzene
o-m-p-Dichlorobenzenes
Trichlorobenzene

Table 4 Combustion products of the coating at 600°

$CO_2 + CH_2{=}CHCl + CH_3{-}CH_2Cl$
CO_2 + 1-butene + isobutylcyanate
Benzene
Methyl isobutyl ketone
Chlorobenzene
Ethylbenzene + o-m-p-xylenes
o-m-p-Chlorotoluenes
o-m-p-Dichlorobenzenes

The last experiment was conducted at 525°, followed by a 800° study (Table 7). It shows that almost complete combustion was obtained at 525°

Table 5 Combustion products of the coating at 400° and 600°, successively

400°	600°
CO_2	CO_2
CO_2	CO_2
Propylene	CO_2 + methyl isobutyl ketone
Chloromethane + propane + CO_2	Methylisobutyl ketone
H_2O + vinyle chloride	Toluene + methyl isobutyl ketone
1-butene	Monochlorobenzene
H_2O + ketone + propanol	
H_2O + acetic acid	
H_2O + acetic acid	
Chloropropane	
Methylethyl ketone	
Butanoic acid	

Table 6 Combustion products of the coating at 400° and 600°, successively

400°	600°
N_2 + CO_2 + little O_2	N_2
CO_2 + H_2O	CO_2
Propane + propene + air + CO_2 + chloroethane	CO_2
Chloroethane + methyl ethyl ketone	Acrylonitrile ($CH_2{=}CH{-}CN$) + imidazole ($C_3H_4N_2$) + propane
Benzene	Chloroethane + methacrylonitrile + 1-butene
Methyl isobutyl ketone	Benzene
Methyl isobutyl ketone	Methyl isobutyl ketone
Methyl isobutyl ketone + toluene	Methyl isobutyl ketone
Chlorobenzene + toluene	Toluene + methyl isobutyl ketone
o-m-p-Dimethylbenzenes (xylenes) + toluene + 2.5 diethylfurane ($C_8H_{12}O$)	Monochlorobenzene
2, 3, 4, 5 Tetramethylfurane	o-m-p-Xylenes + monochlorobenzene
Dichlorobenzene	o-m-p-Chlorotoluenes
Trichlorobenzene	Trichlorobenzene

Conclusions

Some differences appeared in the results obtained by the different techniques. They resulted mainly from the fact that some techniques, e.g. flash pyrolysis and DSC, were employed under dynamic conditions as far as the temperature was concerned, while others, e.g. isothermal TG, were conducted under steady conditions.

These techniques provided useful and complementary data on the degradation and combustion of the coating. Pyrolysis was followed by GC/MS analysis of the degradation products. TG and DSC scanning mode gave the temperature range of degradation

Tabel 7 Combustion products of the coating at 525 and 806°, successively

525°	806°
CO_2	N_2
1-Butene + chloroethane	CO_2
H_2O	Chloroethane + HCl
HCl + isobutyl alcohol	HCl
1-Chloropropane	Benzene
Propylenediamine + acetic acid	Toluene
Acetic acid	
Benzene + N,N-dimethylformamide C_3H_7NO	
Methyl isobutyl ketone	
Toluene	
Butanoic acid	
Chlorobenzene	
5-Cyano-1-hexene + o-m-p-xylenes	
o-m-p-Dichlorobenzenes	
Trichlorobenzene	

and combustion. The results obtained from isothermal TG led to kinetics data for the overall reaction of degradation and combustion.

All these results and more were needed for evaluation of the time at which a substrate reached the ignition temperature when covered with a fire retardant coating.

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Zusammenfassung — Ein schwellender feuerhemmender Überzug kann Ausbreitung und Schäden von Feuer wirksam einschränken und wird zwei Zwecken gerecht: Verhinderung der Ausbreitung von ausgebrochenem Feuer und Schutz der überzogenen Oberfläche vor Hitze- und direkter Flammeneinwirkung. Die beschriebene Komposition quillt und bildet eine Isolationsschicht zwischen der Flammenquelle und dem brennbaren Material, liefert zugleich aber auch eine gewisse Menge von nichtbrennbaren, die Flamme erstickenden primären Zersetzungsprodukten. Die Hauptbestandteile des Überzugs sind Celluloseacetat und -butyrat und HMDI (Desmodur N) für Polyurethan sowie Chlorowax-70 (chlorierte Paraffine) als feuerhemmende Komponente. Dieser feuerhemmende Überzug wurde auf Holzplatten aufgebracht und in einem 2ft-Tunnel getestet, wobei die Flammenausbreitungsgeschwindigkeit gemessen wurde. Der Einfluß von drei interessierenden Parametern wurde untersucht: Typ des benutzten Holzes, Anteil von Chlorowax und Überzugsschichtdicke. Es erwies sich als interessant, die Oxydation des Überzugmaterials mit verschiedenen Techniken zu untersuchen, z.B. durch Schnellpyrolyse und Analyse der Zersetzungsprodukte mittels GC/MS. Verbrennungsuntersuchungen des Überzugmaterials wurden auch mittels DSC und Thermogravimetrie entweder nach der scanning-Arbeitsweise oder unter isothermen Bedingungen ausgeführt. Die bei Pyrolyse und Verbrennung erhaltenen Ergebnisse werden miteinander verglichen.

Резюме — Вспучивание огнестойких покрытий может служить эффективным контролем распространения пламени и вызываемых им повреждений. Во-первых, такое вспучивание ограничивает поверхность распространения пламени к границам уже установившегося пламени, а во вторых — задерживает проникновение тепла и пламени к покрытой поверхности и через нее. Предложенный авторами состав покрытия обеспечивал и расширял изолирующий слой между источником пламени и горящим субстратом, а выделяющееся количество первичных невоспламеняющихся продуктов разложения вызывало гашение пламени. Главными компонентами покрытий являлись ацетат- и бутират целлюлозы и ХМДИ (Десмодур Н) для полиуретана и Хлоровакс (хлорированные парафины) в качестве замедлителя пламени. Такое покрытие было использовано на деревянных панелях и испытано в двухфутовом тоннеле, где была измерена скорость распространения пламени. При этом исследовано влияние трех параметров: тип используемого дерева, процент хлоровакса и толщина покрытия. Изучено окисление покрытия с использованием различных методов, как, например, пламенный пиролиз в атмосфере кислорода с последующим газхроматографическим и масс-спектроскопическим анализом продуктов разложения. Исследование процесса горения покрытия было проведено методом ДСК и термогравиметрии со сканированием или же в изотермических условиях. Проведено сопоставление результатов, полученных методом пиролиза и горения.