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INVESTIGATIONS ON THE FLAME-RETARDATION OF CELLULOSIC FIBROUS MATERIALS

I. THERMAL ANALYSIS

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The thermal behaviours of untreated cellulose (cotton) and samples treated with phosphorus and nitrogen-containing flame-retardants have been studied by means of the derivatograph and quantitative DTA, with the aim of revealing the advantageous features of thermal analysis in the investigation of the flame-retardation of cellulose substrates. The complex thermoanalytical method applied proved to be suitable for the investigation of the efficiency of flame-retardation in parallel with the oxygen index method and the determination of the phosphorus content of the sample. The efficiencies obtained with different methods are in correlation.

A number of research-workers have used thermal analysis, mostly unique methods, such as thermogravimetry and differential thermal analysis, for the investigation of flammability and flame-retardation [1–7]. The application of a complex method, using a derivatograph, is also advantageous, however, since more information can be obtained simultaneously, it makes dynamic measurements possible, the atmosphere surrounding the sample can be varied, and relatively large amounts of sample can be studied.

The thermal decomposition of cellulose is known to be an extremely complex process, which is strongly influenced by the experimental conditions (heating rate, amount of sample, composition of the atmosphere surrounding the sample). By means of gas-chromatography, 37 products were isolated by Schwenker and Pacsu [8], about half of which were identified on the basis of their retention volumes. From the aspect of the flammability of cellulose, the most important product is levoglycosan (1,6-anhydro-β-D-glucose), isolated by Picter and Sarasin [8] as a product of the destructive vacuum distillation of cellulose.

According to Irwine and Oldham [8, 9], the first step in the pyrolysis of cellulose is hydrolysis to glucose, followed by dehydration of glucose to levoglycosan. The measurements of Golova and co-workers [8, 10] have shown that the formation of levoglycosan is not preceded by depolymerization into monomeric units; in contrast, cellulose is depolymerized only to a degree of 200, and this process is accompanied by the evolution of large amounts of volatile products. Levoglycosan is formed thereafter in a second step by dehydration. The polymerization degree of 200 represents the average chain length of cellulose in the crystalline form. Therefore, the initial decomposition, in which side-reactions dominate, takes place in the amorphous phase. This is followed by complete depolymerization in the crystalline state, where the formation of levoglycosan predominates.

Investigations by Honeyman [8, 11] proved that the thermal decomposition of cellulose is a competitive process between depolymerization and the formation of levoglycosan by dehydration. The latter process also requires a thermodynamically unfavourable intermediate transition in which equatorial positions are converted into axial ones. Lewis acids (e.g. $ZnCl_2$) catalyse depolymerization at temperatures lower than that of the equatorial-axial transition.

As shown by the investigation of Chatterjee and Conrad [12], the thermal decomposition of cellulose starts with a random chain scission, whereupon the chain-end bearing the oxygen of the glycosidic bond is stabilized by removing a proton from the OH group of an adjacent monomer. Owing to deprotonation an unstable transition product is formed again, which splits off a levoglycosan molecule from the chain-end. A free radical mechanism was suggested by Martin [8] too, as one possibility for the thermal decomposition of cellulose. However, it has been calculated by Esteve [8] that the activation energy of the pyrolysis of cellulose is much lower than the energy required for the free radical process. It can therefore be assumed that levoglycosan is formed in the solid phase.

To date about a thousand compounds have been synthesized which have flame-retardant effects and decrease the rate of combustion. These compounds generally contain phosphorus, nitrogen, antimony, boron or halogens. On cellulose substrates the retardants which contain phosphorus, nitrogen, and optionally halogen, are the most widespread. These substances are commercially available under the names Pyrovatex CP, THPOH and THPC. The latter two compounds are always used in combination with nitrogen-containing bases. In the process of retardation all three retardans are presumably present in the form of phosphoric amide. The various types of flame-retardants exert their effects in slightly different ways. Flame-retardation is due partly to physical, and partly to chemical processes. A substantial role most be played by chemical inhibition reactions, which may proceed in the gas or the solid phase [13, 14]. Inhibitors acting in the gas phase suppress the propagation of the flame itself, thereby decreasing the rate of already-existing combustion [14]. The other group of inhibitors, acting in the solid phase, suppress the formation of combustible components [15, 16].

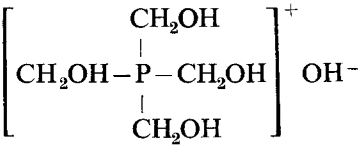
This work aims at investigating the thermal properties of cellulose substrates, flame-retardants and fibrous materials treated with flame-retardants, by complex thermoanalytical methods and quantitative DTA measurements. A further aim is to test the applicability of thermoanalytical methods in this field. The efficiency of flame-retardation is studied by thermoanalytical, and in part by other analytical methods.

Experimental

Materials

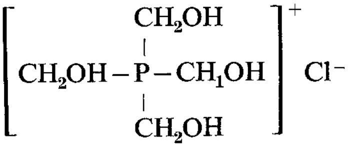
As substrates, fibrous materials of 100% cellulose content were applied. A wide choice of flame-retardants were tested, including inorganic $(NH_4)_2HPO_4$, and some organic compounds simultaneously containing phosphorus and nitrogen. Of the latter type, the following flame-retardants were available: THPOH + amide, THPOH + ammonia, THPC + urea + Na_2HPO_4, and Pyrovatex CP.

The trade names in the above list correspond to the following chemical structures.



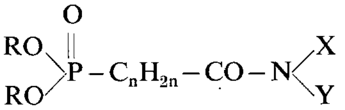
$$\left[\begin{array}{c} CH_2OH \\ | \\ CH_2OH-P-CH_2OH \\ | \\ CH_2OH \end{array}\right]^+ OH^-$$

Tetrakis(hydroxymethyl)
phosphonium hydroxide
THPOH



$$\left[\begin{array}{c} CH_2OH \\ | \\ CH_2OH-P-CH_1OH \\ | \\ CH_2OH \end{array}\right]^+ Cl^-$$

Tetrakis(hydroxymethyl)
phosphonium chloride
THPC



R = alkyl
X = CH_2OH
Y = CH_2OH, H

Pyrovatex CP

Methods

The complex thermoanalytical measurements were performed with a MOM derivatograph, and quantitative DTA with a Du Pont 990 Thermal Analyzer. Oxygen index (OI) was measured with a Stanton Redcroft FTA Flammability Unit.

Complex thermoanalytical measurements

The measurements were carried out under the following experimental conditions. Sample weight: 100 mg, ceramic crucible, empty reference crucible, heating rate: 5°/min, static gas (air) atmosphere.

Figure 1a shows the thermoanalytical curves of pure cellulose substrate. It can be seen from the TG and DTG curves that the weight loss starts at 50°, indicating the desorption of adsorbed moisture, which terminates at 120°. The main decomposition process starts at 225°, its rate reaching a maximum at 330° (DTG), and this is followed by a further decomposition step which causes a 100% weight loss by 500°. According to the DTA curve, the loss of adsorbed water is endothermic, whereas the thermal decomposition of cellulose is a strongly exothermic process.

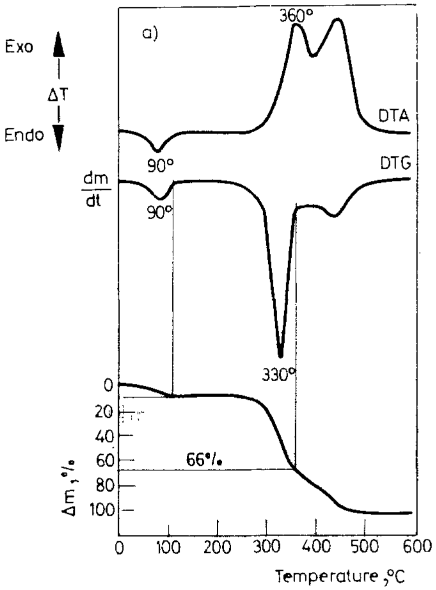


Fig. 1a. Thermoanalytical curves of pure cellulose substrate in air

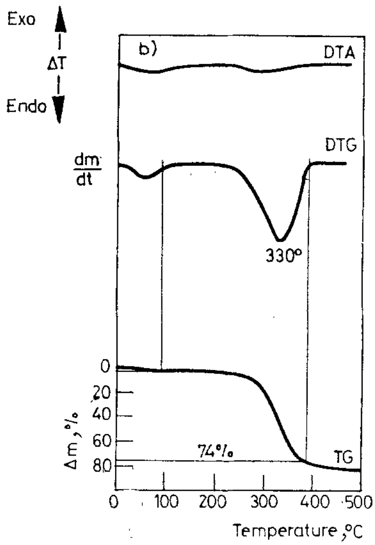


Fig. 1b. Thermoanalytical curves of pure cellulose substrate under inert gas atmosphere

Figure 1b shows the decomposition of the same cellulose substrate under an inert gas atmosphere (30 l/h of nitrogen). The weight loss is still ca. 80% by 500°, but the process is slightly endothermic. Consequently, the exothermic decomposition under the given conditions requires atmospheric oxygen.

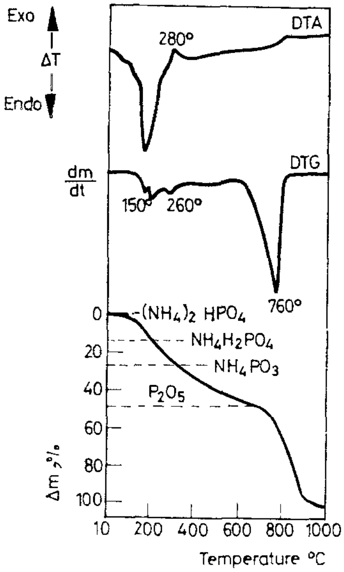


Fig. 2. Thermoanalytical curves of $(NH_4)_2HPO_4$

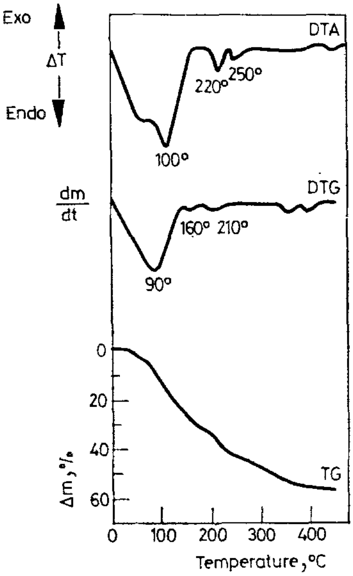


Fig. 3. Thermoanalytical curves of Pyrovatex CP

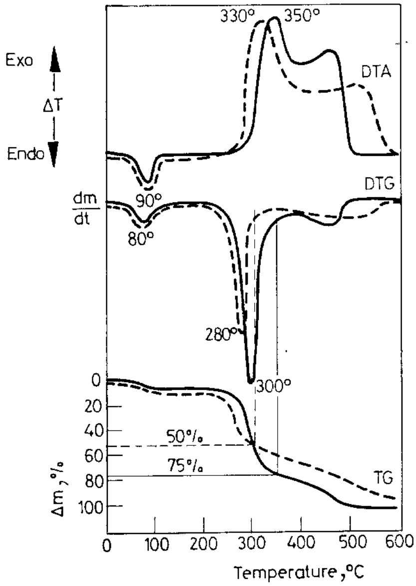


Fig. 4. Thermoanalytical curves of pure and with $(NH_4)_2HPO_4$ retarded cellulose

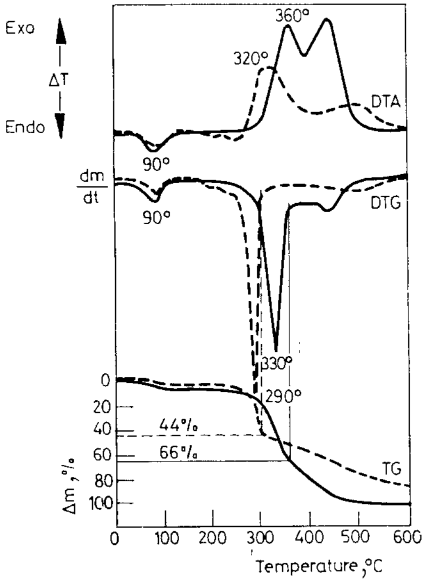


Fig. 5. Thermoanalytical curves of pure and with Pyrovatex CP retarded cellulose

Figure 2 shows the thermal decomposition of $(NH_4)_2HPO_4$. By the loss of 1 molecule of ammonia, the compound is first converted to $NH_4H_2PO_4$, and it then melts at 170°. The weight loss corresponding to the DTG peak at 260° indicates the loss of 1 molecule of water, suggesting the formation of $(NH_4)_2H_2P_2O_7$. This compound loses a further water molecule, being converted to metaphosphate, which recrystallizes at 280° to yield a water-insoluble glassy melt (see DTA). With further increase of temperatures, NH_3 and H_2O are released, and the substance is finally converted to P_2O_5, which evaporates at higher temperatures [17].

The thermoanalytical curves of Pyrovatex CP are shown in Fig. 3. According to the curves the sample decomposes at low temperatures, and 58% weight loss can be measured by 450°. Decomposition is always endothermic.

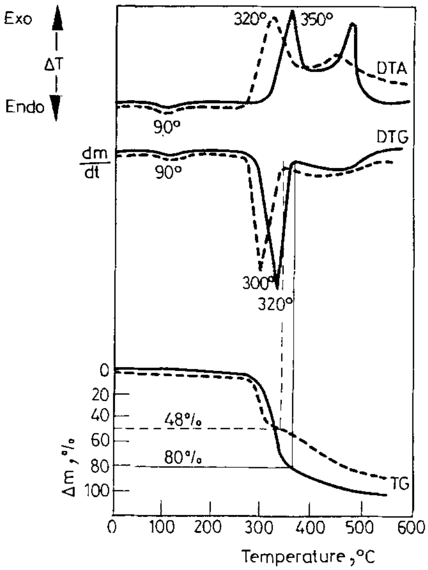


Fig. 6. Thermoanalytical curves of pure and with THPOH + amide retarded cellulose

The other flame-retardants were not available in pure form, and thus their thermoanalytical curves were not measured.

After the thermal analysis of pure substrate and flame-retardants, the decomposition of substrate treated with flame-retardants was studied. For the sake of better comparison, the thermal curves of untreated and treated samples were redrawn in the same diagram.

Figure 4 illustrates the effect of treatment with $(NH_4)_2HPO_4$. The thermal decomposition curve clearly indicates the changes with respect to the untreated sample. After treatment, the thermal stability is slightly decreased, but at higher temperatures the TG curve of the treated sample always runs above that of the untreated

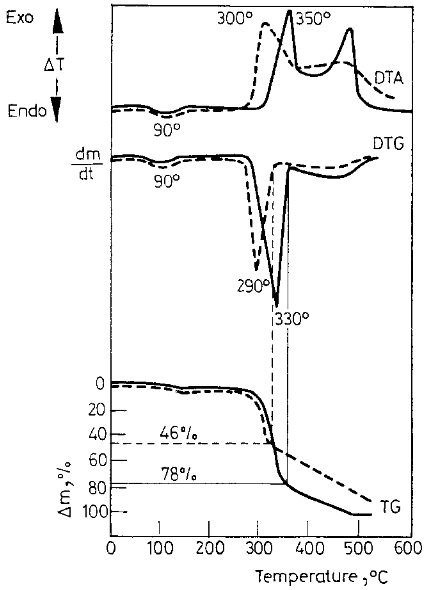


Fig. 7. Thermoanalytical curves of pure and with THPOH + NH_3 retarded cellulose

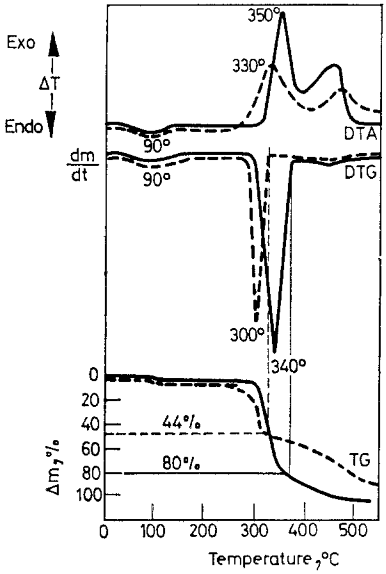


Fig. 8. Thermoanalytical curves of pure and with THPC + urea + Na_2HPO_4 retarded cellulose

substance. Accordingly, the treatment decreases the amount of potentially flammable gases occurring in the gas phase between 250 and 500°. When compared at a characteristic point, the end of the main decomposition process, there is a 25% difference in weight loss.

The further Figures show the effects of phosphorus and nitrogen-containing organic flame-retardants. The first example is a phosphoric acid derivative, Pyrovatex CP, whereas the other retardants consist of separate phosphorus and nitrogen-containing components, which also presumably form phosphoric amide upon thermal effects [15, 16].

The thermal decomposition of cellulose treated with Pyrovatex CP (Fig. 5) starts at 150°. The change in enthalpy relating to the decomposition between 275 and 600° is smaller, and this amount of heat is released at a lower rate than in the case of untreated cellulose. Figures 6, 7 and 8 show essentially the same feature as those obtained with Pyrovatex CP, with some minor differences in the DTA and DTG peak positions.

Quantitative DTA measurements

Our observations concerning the heat evolved obtained from complex measurements have been made more accurate by further thermal methods. Quantitative DTA measurements permit numerical information to be obtained on the enthalpy changes accompanying the thermal decomposition of cellulose under the given experimental conditions. Figure 9 shows the quantitative DTA curve of a ca. 10 mg sample. In the case of untreated cellulose the main decomposition takes place between 275 and 500°, with $Q = 584$ mcal/mg. The corresponding change in the treated sample takes place between 250 and 600°, with $Q = 471$ mcal/mg.

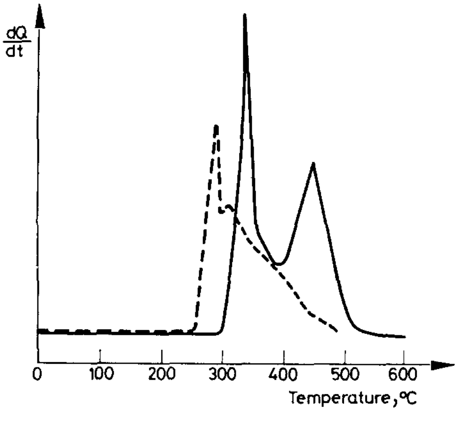


Fig. 9. QDTA measurement of pure and retarded cellulose

Investigation of flammability and flame-retardation

The phosphorus content of the sample unambiguously characterizes the amount of flame-retardant applied to the sample, i.e. the flame-retardation. For this purpose, phosphorus was determined by the method of Bernhardt and Wreath [20]. Phosphorus-containing textiles were destroyed with a mixture of 25 ml HNO_3 and 20 ml $HClO_4$. The resulting colourless solution was made up to 100 ml, and 5 ml portions were reacted with ammonium molybdate in sulfuric acid. As the complex obtained is soluble in acetone, 12.5 ml of acetone was added to the sample, and the solution was made up to 25 ml with distilled water. The absorbance of the resulting yellow solution was measured at 430 μm with a Spectromom-204 photometer. After establishment of the calibration curve shown in Fig. 10, the results given in Table 1 were obtained (the amount of P is expressed as P_2O_5 content).

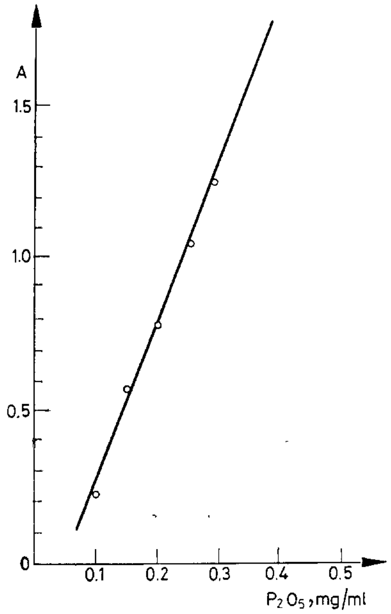


Fig. 10. Calibration curve of phosphorous measurement

To determine the precision of measurement, five parallel measurements were made. The greatest difference of the individual results from the average was 0.1 w%. Since this is smaller than the differences arising from inhomogeneities of the sample, the Bernhard-Wreath method was accepted as suitable for the determination of phosphorus content.

For the determination of flammability and flame-retardation, the oxygen index (OI) method was also applied in addition to the conclusion drawn from complex

Table 1

FR compound	Substrate	P_2O_5, w%
THPOH + amide	linen	6.0
THPOH + amide	flannel	6.1
THPOH + NH_3	flannel	10.0
THPC + urea + Na_2HPO_4	linen	6.2
Pyrovatex CP	linen	3.0

thermoanalytical investigations. The OI method, developed by Fenimore [19], has become increasingly popular in recent years. The OI is a dimension less number which gives the volume ratio of oxygen in the oxygen-nitrogen mixture in which the sample is just able to burn:

$$\mathrm{OI}\ \% = \frac{100 \times O_2}{O_2 + N_2}$$

where O_2 and N_2 are the volume ratios of oxygen and nitrogen, respectively.

The OI-s of the samples studied are given in Table 2.

As can be seen from the results, linen treated with THPOH + amide is the least flammable, whereas untreated flannel is the most flammable.

Table 2

Sample	OI, %
Untreated flannel	17.5
Untreated linen (Hungarian)	18.6
Untreated linen (USA)	19.0
Linen treated with 3% Pyrovatex CP	29.2
Flannel treated with 6% THPOH + amide	29.5
Flannel treated with 10% THPOH + NH_3	29.8
Linen treated with 6% THPC + urea + Na_2HPO_4	30.7
Linen treated with 6% THPOH + amide	34.5

Table 3

Flame-retardant	Difference in OI values
Pyrovatex CP (3%)	29.2 − 18.6 = 10.6
THPC + urea + Na_2HPO_4 (6%)	30.7 − 19.0 = 11.7
THPOH + amide (6%)	29.6 − 17.5 = 12.1
THPOH + NH_3 (10%)	29.8 − 17.5 = 12.3
THPOH + amide (6%)	34.5 − 19.0 = 15.5

Table 4

FR compound	Difference in TG, %
Pyrovatex CP	22
THPOH + amide (6%)	31
THPOH + ammonia (10%)	36
THPC + urea + Na_2HPO_4 (6%)	32

OI data can be used as a first approximation to characterize flame-retardation numerically. When the OI of an untreated sample is subtraced from that of the treated sample, a numerical estimate of the flame-retardation is obtained (Table 3).

Results

On the basis of the thermoanalytical measurements it can be stated that the thermal decomposition of cellulose, under the given experimental conditions, in air, takes place in two steps. The main decomposition process, which has a maximum rate at 330° (DTG), is strongly exothermic. As a result of the flame-retardant additives investigated, which contain phosphorus and nitrogen, the thermal stability of samples decreases slightly, and the amount of potentially flammable gases released into the gas space decreases by an average of 25–30%. According to quantitative DTA, the exothermic character of the reaction decreases by ca. 20% after treatment with THPOH + ammonia.

We have found the method of dynamic thermal analysis to be applicable for the investigation of flame-retardation, since it makes possible the study of the changes occurring with increasing temperatures, thereby modelling real fire cases.

It can be stated in general that the temperature characteristic of the thermal stability of the sample can be read directly from the TG and DTG curves, and the complete process of decomposition, including the formation of incombustible residues, can be followed. It is also possible to calculate the percentage weight loss corresponding to any moment or temperature, which is equivalent to the possible maximum flammable material released into the gas space. With a derivatograph by measurement of the DTA curve, a qualitative picture can be obtained on the endo- or exothermic natures of the processes. Quantitative information can be obtained by means of a special DTA or DSC instrument about the heat evolved. If the atmosphere in the environment of the sample is changed, or the measurement is run under its own gas atmosphere, the reactions taking place in various environments and at equilibrium pressure and temperature can be studied.

From the thermal investigations two types of information have been obtained. The weight losses corresponding to the end-points of the main decomposition processes of untreated and treated samples are characteristic of the flammability of samples, whereas the difference between these weight losses characterize flame-retardation. Presumably, the differences between the TG curves of a substrate treated with the same amounts of flame-retardants which contain phosphorus in chemically different forms may be used to compare the efficiencies of various flame-retardants. According to the literature [20], levoglycosan, the compound responsible for the flammability of cellulose, is formed in the main decomposition process of cellulose. Due to this fact, the weight loss corresponding to the end of the main decomposition process was accepted as a measure of flammability.

As the data of Table 4 indicate, the most efficient flame-retardation was obtained with 10% THPOH + NH_3. A comparison of THPOH + amide and THPOH + NH_3 system shows that the former has the higher specific efficiency. Whereas a treatment with 6% THPOH + amide causes a difference of 31%, if in a relatively narrow region a linear relationship is assumed to hold between phosphorus content and flame-retardation, 6% THPOH + NH_3 would also cause a difference of 31%. The lower efficiency of the THPOH + NH_3 system is presumably due to the fact that a part of the NH_3 is released during thermal treatment, and thus only a smaller amount of phosphorus amide may be formed.

Flammability and flame-retardation can be estimated numerically by measuring OI (Tables 2 and 3). It can be said that the greater the difference in OI after the treatment, the more efficient the flame-retardant additive. Similarly to the results of thermal measurements, it has been found that the most efficient combinations are THPOH + NH_3 and THPOH + amide. Upon the effect of ca. 10% THPOH + NH_3, the OI increases by 12.3, while in the case of 6% THPOH + amide the difference is 12.1. A treatment with 6% THPOH + NH_3 would have caused an increase of ca. 7.4 OI units.

Consequently, in characterizing flammablity and flame-retardation, the data obtained with complex thermal analysis are in correlation with the results of OI measurement.

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RÉSUMÉ — Dans le but de montrer les avantages que présente l'analyse thermique pour l'étude de l'effet des ignifuges sur les substrats cellulosiques, le comportement thermique de la cellulose non traitée (coton) et d'échantillons traités par des ignifuges contenant du phosphore ou de l'azote a été étudié à l'aide d'un Derivatograph et par ATD quantitative. La méthode d'analyse thermique complexe appliquée s'est révélée bien adaptée à l'étude de l'efficacité de l'ignifugation, par comparaison avec les examens effectués en parallèle avec la méthode de l'indice d'oxygène et par dosage de la teneur en phosphore de l'échantillon. Les valeurs de l'efficacité obtenues avec les différentes méthodes sont en corrélation.

ZUSAMMENFASSUNG — Das thermische Verhalten unbehandelter Zellulose (Baumwolle) und mit phosphor- und stickstoffhaltigen Imprägniermitteln behandelter Proben wurde mit Hilfe des Derivatographen und der quantitativen DTA untersucht, um die vorteilhaften Eigenschaften der Thermoanalyse bei der Untersuchung der flammensicheren Imprägnierung von Zellulosesubstraten zu zeigen. Die angewandte komplexe thermoanalytische Methode erwies sich zur Untersuchung der Wirksamkeit der Imprägnierung im Paralleleinsatz mit der Sauerstoffindex-Methode und der Bestimmung des Phosphorgehalts der Probe als geeignet. Die mit den verschiedenen Methoden erhaltenen Wirksamkeitswerte stimmten gut überein.

Резюме — Изучено термическое поведение необработанной целлюлозы (хлопка) и ее образцов, обработанных фосфор- и азотсодержащими ингибиторами пламени с помощью дериватографа и количественного ДТА, с целью установления преимущества метода термического анализа для исследования замедления пламени на образцах целлюлозы. Использование такого комплексного термоаналитического метода показало, что он, совместно с методом кислородного индекса, приемлем для исследования эффективности замедления пламени и определения фосфорсодержащего образца. Закономерности, полученные различными методами, хорошо коррелируются.