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THERMOANALYTICAL STUDIES OF COMBUSTION OF CELLULOSICS AND ACTIVITY OF FIRE RETARDANTS

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TG, DTG and simultaneous DTA were used to monitor the thermal decomposition processes of cellulose in nitrogen or in an oxidative atmosphere. Volatile products and solid residues formed during decomposition were analyzed to obtain additional information for elucidation of the thermal curves. An indication of possible flaming or smoldering combustion is discussed. The maximum weight-loss rate, the percentage amount of the residue at the final temperature, and the exothermic peak areas (DTA) could be considered as suitable criteria for the flammability of cellulosics and the activity of flame retardants. The formal kinetic parameters evaluated from the thermogravimetric measurements correspond to the limiting oxigen index (LOI) values. New observations were made using a combination of thermal analysis and LOI techniques. LOI — smoldering or LOI — flaming are mathematically determined from the plot of weight-loss rate versus oxygen concentration.

Methods of thermal analysis (TG, DTG, inverse TG, DTA and DSC) are often used for the study of the processes of combustion and flammability of polymers from various aspects, as is shown in Table 1.

Thermoanalytical methods can give only partial information about the course of a burning process, allowing study of individual stages, as for instance the active thermolysis and glowing combustion. By thermoanalytical techniques it is difficult to obtain data on the process of flaming combustion, as this is difficult to simulate in terms of thermal analysis, using relatively small amounts of sample. When the usual methods of thermal analysis (small amounts of sample and considerable gas flow) are used, flaming combustion is not observed. Further difficulties are brought about by the fact that burning is a complex phenomenon involving appreciable overlapping of exothermic and endothermic processes. For this reason it is not easy to evaluate accurately in particular DTA, or DSC curves. Despite these facts, the combination of thermoanalytical methods and other experimental techniques (spectral methods of separation and identification of volatile products) may yield valuable data about the burning process, the flammability of cellulosics and the effect of flame retardants in particular. In searching for more efficient retarding systems, the thermoanalytical techniques have proved to be the most satisfactory because they allow not only determination of the relative efficiency of retardants but even elucidation of the retardation mechanism.

Table 1

Thermoanalytical study of processes of combustion and effect of fire retardants

Group and score	Aspects	Methods	References
i	Partial information		
E	— active thermal, degradation	TG, DTG invers TG	1—5
D	— ignition temperature	DTA	7
E	— ignition temperature	DTA+T—signal	8
VD	— heats of gasification (pyrolysis) depolymerization	DSC	6
P	— heat of glowing combustion	DTA	4
ii	Particular study of the course of process		
D	— kinetic parameters	TG, DTG, DTA	9—11, 29
D	— chemisms of reactions	TG, DTG, and further (DTA) analysis	11—15, 25
iii	Effect of chemical and physical structures		
E	— elementary composition	calorimetry TG, DTA, DSC	1—4
D	— full chemical structure DP, composites	TG, DSC	1—5, 19
P	— crystallinity, porosivity	TG, DTG, DTA	4, 10
VD	— geometry	TG	4
iv	Effect of external conditions		
VD	— heat flux	DTA, TG various heating rate	4
VD	— gas flow	various flow rate TG, DTA	4
P	— oxygen content	TG, DTG	17, 18
v	Efficiency of retardants		10, 18—30
E	— amount of additives	TG	10, 19
P	— chemical composition	TG, DTA, DTG	20, 25, 26
P	— synergism	TG, DTA	20, 21
vi	Mechanisms of action of retardants		
P	— chemical action	TG, DTA and further analysis	9—15, 22—30
D	— physical action	DTA, TG	4, 26, 30
P	— action in condensed phase	TG, DTG, DTA	9—15, 22—30
VD	— action in flame	DTA	4, 30

E — easy; D — difficult; VD — very difficult; P — possible

Experimental

Materials

Two forms of cellulose were used. Prehydrolyzed kraft pulp and cotton cloth. Prehydrolyzed kraft pulp was produced commercially from beech wood and gave the following analyses: α-cellulose 96.2%, pentosans 3.05%, ash 0.05%, DP 850. Cotton cellulose free of pectic substances contained 99.6% α-cellulose and 0.18% ash, with DP 3050. The impregnated, cyanoethylated and grafted samples were prepared by means of the techniques described previously [23].

Spruce wood (Picea excelsa L.), spruce wood particle board, and mineral-cellulosic fiber board were used as samples having dimensions of 0.4 × 0.8 × 15 cm or treated sawdust (0.2 – 0.3 mesh) for thermal analysis; they were conditioned to a dryness of 90 – 93%.

Thermal analysis

All measurements were made in a dynamic atmosphere of air or nitrogen (71 · h^{-1}) using a Mettler Thermoanalyser 2, at a constant heating rate of 10° min^{-1}; Pt/Pt + Rh thermocouples with Al_2O_3 were used as standard for DTA.

Combination of the L.O.I. test with thermal analysis

The instrument for the L.O.I. test and the derivatograph (MOM, Budapest) were combined. The main features of the apparatus are shown in Fig. 1.

The sample 4 was suspended in glass chamber 1 with the aid of a ceramic thermocouple rod serving as sample holder 2. The nitrogen and oxygen mixture

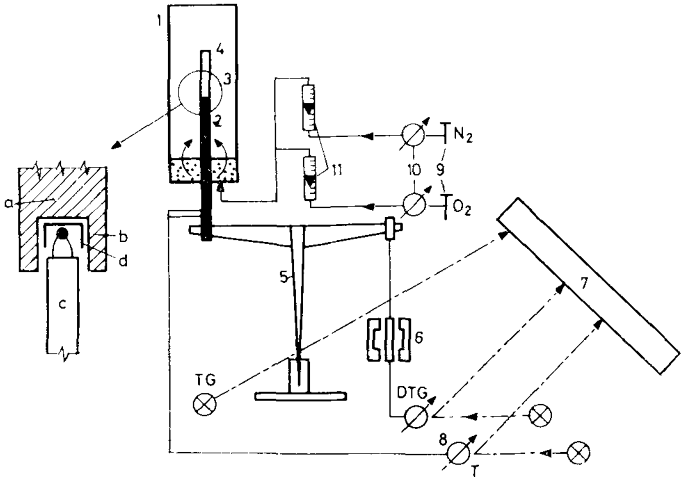

Fig. 1. General arrangement of the apparatus: (1) glass chamber; (2) thermocouple rod/sample holder; (3) thermocouple; (4) sample; (5) balance; (6) induction coil; (7) photographic paper for registration; (8) galvanometers; (9) on, off valves; (10) flow valves; (11) flow meters

was passed through the glass chamber in the same manner as in the oxygen index test [31]. During the burning process the weight-loss of the sample (TG and DTG) and the temperature rise were recorded using the pertinent parts 5, 6, 7 and 8 of the derivatograph. For this combined test samples of definite size (0.2 – 0.4 × 0.8 × × 15 cm) were used.

Thermooxidation

The oxygen consumption on heating samples of cellulose and polypropylene was measured by means of the equipment described previously [32].

Results and discussion

Thermoanalytical study on the course of burning of cellulose

It is generally believed [11 – 16] that several primary reactions take place when cellulose is heated in an air atmosphere, e.g. thermooxidation, dehydration, depolymerization with glycosan formation (Fig. 2).

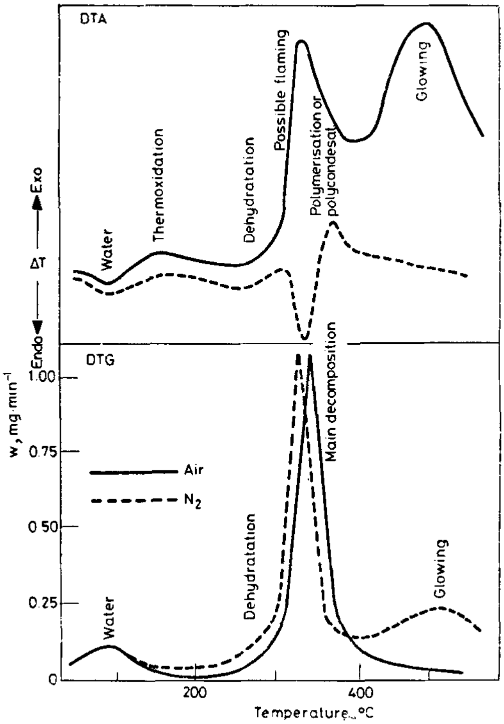

Fig. 2. TG, DTG and DTA curves of cellulose in nitrogen -------- and oxygen ——— atmosphere

Thermooxidation proceeds as a peroxidic radical reaction. During this reaction (at a temperature of 120—250°) some uptake of oxygen can be observed when a suitable apparatus is used [32]. From DTA curves it is very complicated to conclude the course of thermooxidation, because exo- and endo- effects (dehydration) overlap. The changes in weight that were observed are very small, and the effect of oxygen uptake is compensated by the weight loss caused by decomposition of the peroxides and hydroperoxides formed and by dehydration. Another reaction which is also difficult to monitor by thermal curves is dehydration of untreated cellulose. TG curves (Fig. 2) show slow active degradation (at 220—280°) and on DTA a slight endothermic effect is observed. The volatile material consists mainly (about 90 per cent) of water. From both the IR spectra of the residues [11, 23] and the bromine consumption it can be concluded that unsaturated structures are formed during dehydration [11, 12]. The most important information about the flam-

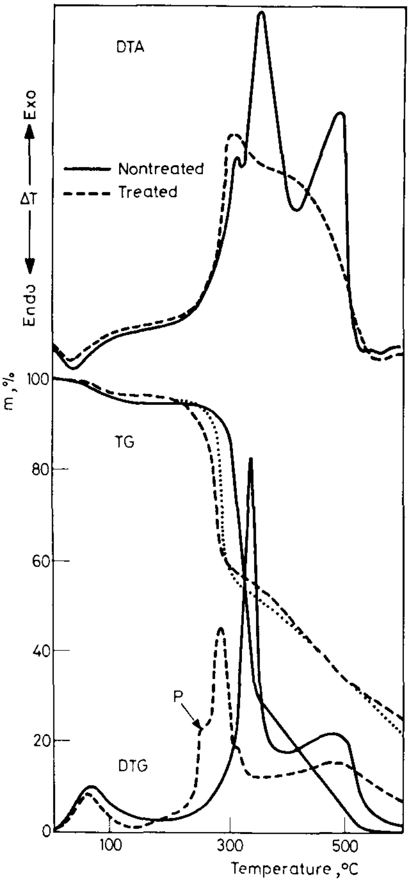

Fig. 3. Thermal curves of cellulose fabrics treated with and non-treated

mability of cellulose is given by TG and DTG curves in the temperature range 280–360°. In particular, the maximum rate of decomposition is equal to the rate of flammable volatile (glycosan) formation and seems to be an important criterion for the flammability of cellulosics. In the same temperature range the flaming combustion of cellulose can arise. The observation of flaming depends mainly on the concentration of volatiles formed. The process of flaming combustion is difficult to simulate in thermal analysis when very small amounts of a sample and a considerable gas flow are used. The glowing combustion of cellulose takes place in the temperature range 400–600°. This is observed only in an oxidative atmosphere (Fig. 2). The char is converted to ash during this process.

Cellulose treated with N-methylol phosphonopropionic amides is a material with well-reduced flammability according to the LOI values, ignition temperature, mass, burning rate, etc. Thermal curves for original and treated samples (Fig. 3) show considerable differences. The maximum rate of weight loss is much lower for treated samples than for original cellulose. The residue can amount to 23 percent of the weight of treated sample, while for non-treated cellulose only a small amount of ash (less than 1%) is observed. The exothermic areas (both for flaming and for glowing) are reduced in the case of treated samples.

The mechanism of fire retardancy of cellulose treated with N-methylol phosphonopropionic amides has been studied by numerous authors [14, 20, 25, 33–35]. According to our recent results [20], this is too complicated and therefore the complex action of phosphorus and of formed amino groups should be considered in the explanation. The maximum rate of volatilization of treated cellulose can be reduced not only by dehydration. After the acidic hydrolysis of treated samples (when the phosphorus content is diminished substantially), DTG still shows an essentially reduced maximum weight-loss rate (Fig. 2). The maximum weight-loss rate can be reduced by the different action of retardants of cellulosics [23] (Fig. 4). This conclusion confirms that various changes occur in the DTG curves of treated celluloses. The cross-linking reactions play an important role in the efficiency of some treatments. From the practical point of view it is important that the maximum weight-loss rate may be used to evaluate the efficiency of fire retardants of cellulosics.

Figure 5 shows a plot of the dependence of the formal activation energy (calculated from DTG) upon the limiting oxygen index (LOI) for various samples of treated cellulosics. The values of the activation energies are proportional to the results of the LOI – flammability test.

Thermoanalytical study of combustion and fire retardancy of wood

TG, DTG and DTA curves of spruce wood (Fig. 6) show a similarity to the thermal curves obtained for pure cellulose (Fig. 2).

However, hemicelluloses are more reactive wood components and their active degradation begins at a lower temperature. Both char formation (about 35 percent) and the glowing combustion of wood occur to a larger extent than the flaming process.

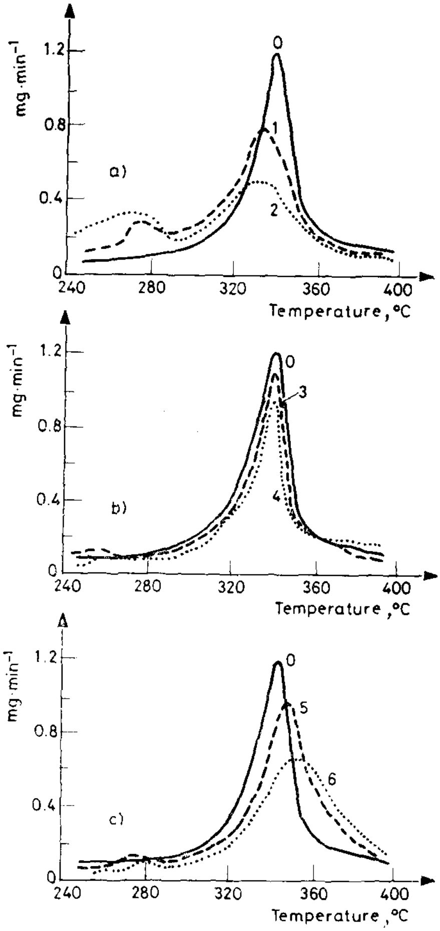

Fig. 4. Effect of various types of cellulose fabrics treatment on the DTG curves (o) without treatment; (a) impregnated with: (1) 5% $NH_4H_2PO_4$, (2) 10% $NH_4H_2PO_4$; (b) cyanoethylated; (3) 0.33 DS, (4) 0.55 DS; (c) grafted with acrylonitrile; (5) nitrogen = 12.5%; (6) nitrogen = 15.2% wt

Until now, inorganic fire retardants have mostly been used for the fire protection of wood and wooden products. TG and simultaneous DTA give a possibility to determine the efficiency of inorganic salts as well as their classification into several groups [9, 25] (Fig. 7).

Suitable parameters for the evaluation of wood flammability are:

- the maximum weight-loss rate (DTG),
- the percentage of the residue at the final temperature (500°; TG),
- the exothermic peak areas (DTA).

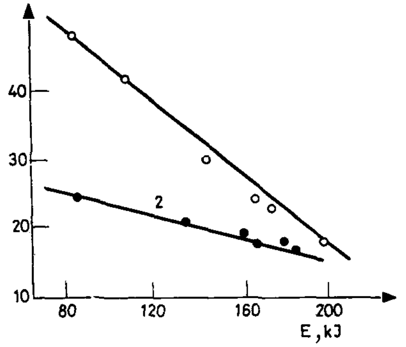

Fig. 5. The plot of limited oxygen index and activation energy calculated from DTG for spruce wood treated with: (1) 15% water solution of $NH_4H_2PO_4$ and for cotton cellulose grafted with acrylonitrile (content of nitrogen 3.1–16.2%) —●—●—●—●— (2)

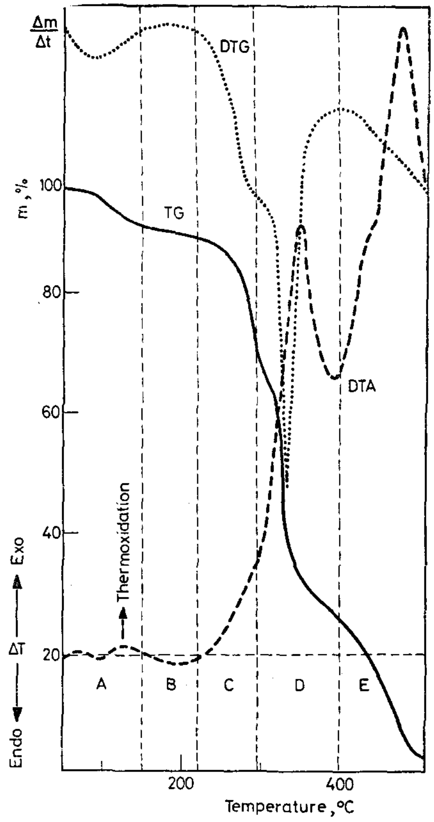

Fig. 6. Thermal curves of spruce wood (in air flow)

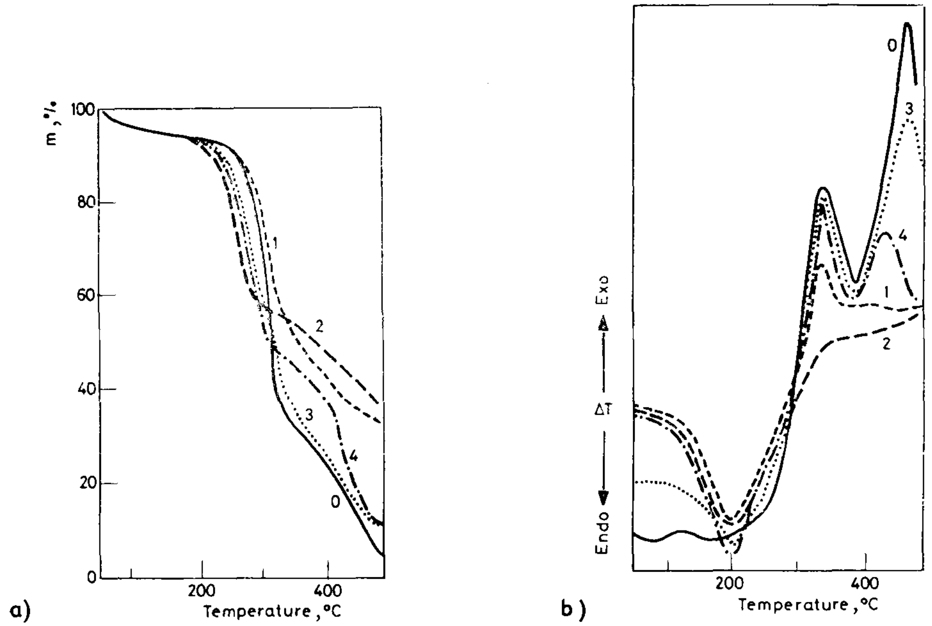

Fig. 7. TG and DTA curves of spruce wood impregnated with various inorganic salts; o — nontreatment; 1 — $Na_2B_4O_7$, 2 — $(NH_4)H_2PO_4$, 3 — NaCl, 4 — K_3PO_4

In Table 2 the above parameters are shown for wood and wood impregnated with various inorganic salts.

The thermoanalytical data correspond to the results of the evaluation of flammability by the usual standard tests (LOI, ČSSR, standard 73 0853). The particular advantage of thermoanalytical methods lies in the possibility of considering the retardancy mechanism for the inorganic salts used. The thermal curves and the

Table 2

The effects of inorganic salts on the parameters of flammability for spruce wood

Sample treated with	W_{max} mg/min	Residue at 500°, %	Relative exothermic areas*	LOI	CO_2/CO
Non-treated wood	1.31	3	1.00	24	5.1
$Na_2B_4O_7$	0.60	32	0.37	42	1.5
$NH_4H_2PO_4$	0.52	33	0.11	55	1.4
NaCl	1.07	8	0.97	26	4.5
K_3PO_4	0.79	10	0.81	27	3.7

* The relative areas of exothermic peaks were calculated from the values for the appropriate parts of the curves, divided by the value determined for non-treated wood.

additional analysis permit one to estimate if an inorganic salt acts chemically or if its efficiency is only physical in nature. There are several possibilities of action [27]:

a) in the initial stage of the process
   - a change of thermal conductivity and thermal capacity,
   - consumption of heat (for melting, sublimation, evaporation, or for chemical reaction),
- inhibition of self-ignition process (by termination of autooxidation);

b) in thermolysis
changes in the course of the process leading to the production of less flammable volatiles (catalysis of dehydration),
- inhibition of homolytic rupture of glycosidic bonds (glycosan formation),
- suppression of active thermolysis;

c) in flaming combustion
- possibility of dilution of the flammable mixtures,
- termination of flame reaction;

d) in glowing combustion
suppression of attachment of oxygen,
- termination of carbon oxidation (changes in CO/CO_2 formation).

In our opinion the effect of $NH_4H_2PO_4$ can be classified according to the cases shown in *a, b, c* and the action of $Na_2B_4O_7$ according to *a, d.* The flaming or smoldering combustion of cellulosics is strongly dependent on the oxygen concentration.

The effect of oxygen concentration on the fire propagation of cellulosics

For this purpose thermal analysis was used [18]. Differences appear in the course of the TG, but they are small. This results from the fact that the sample sizes used are very small. When reduced sizes of samples are used, the LOI values are diminished [17]. Differences in the course of both flaming and glowing combustion are diminished too, since a great excess of oxygen is present. Using samples of definite dimensions and the apparatus is in Fig. 1, we have obtained the results given in Figs 8, 9 and 10.

The oxygen concentration was equal to or higher than that at the LOI. The effect of oxygen upon the flaming combustion of the samples of defined dimensions is noticeable and can be evaluated quantitatively [4, 18]. This provides information on the increased burning rate (up to an explosion), which may be important in the case of some types of solid materials [4, 18].

Both the recorded TG and the temperature curves provide valuable information about non-flaming combustion (smoldering) of some solid materials in an oxygen-rich atmosphere. Figure 8 shows the results obtained from the investigation of the burning process of wood. In brief, after flaming ignition the flame was extinguished

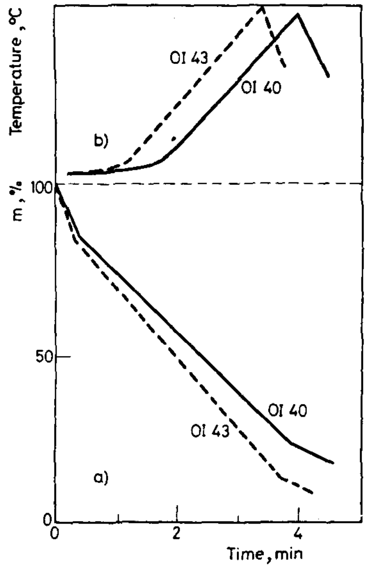

Fig. 8. Smoldering of spruce wood at different oxygen concentration (OI) monitored by TG (a) and temperature-raise curve (b)

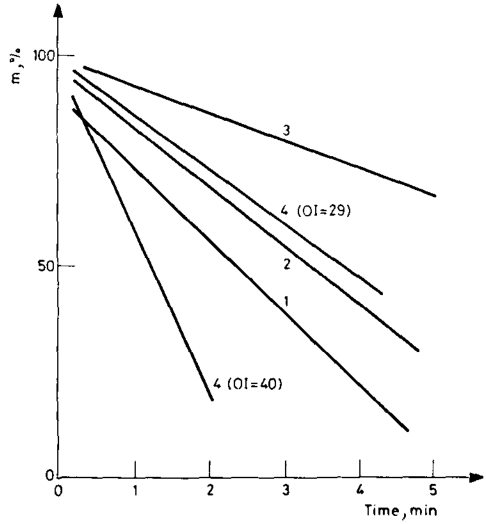

Fig. 9. Weight-loss during smoldering of various solid materials at certain oxygen concentration; 1 — spruce wood, 2 — wood particle board, 3 — mineral cellulosic fiber board, 4 — commercional cigarette (Czarda)

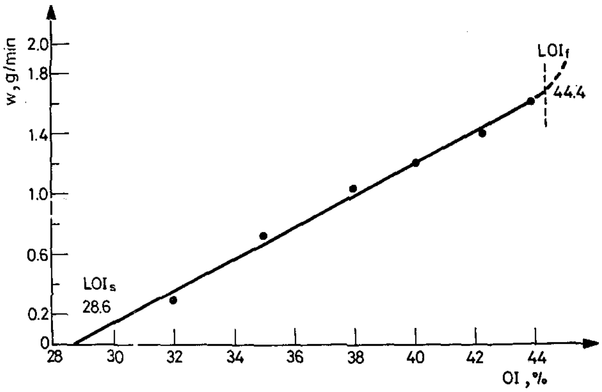

Fig. 10. The plot of smoldering rate and oxygen concentration LOI$_S$ — limited value of OI for $W \to o$; LOI$_f$ — limited value of OI for spontaneous flaming

by means of a short-term stream of carbon dioxide and the process of smoldering, which proceeded spontaneously, was observed. At an oxygen concentration higher than the LOI a number of cellulosic samples are spontaneously oxidized in the solid state. The rate of spreading of non-flame combustion is constant for a long time and is proportional to the oxygen concentration [18]. The simple surface combustion which was observed during these experiments can be applied for the theoretical treatment similarly as was described for the combustion of wood charcoal [36].

Another advantage of the test modified in our laboratory consists in the fact that it permits a limited oxygen concentration to be determined more accurately, particularly for the material where the visual observation of flaming is difficult. The weight, loss on the smoldering of these materials was recorded continuously (Fig. 9) and thereby the constant rate of the process could easily be determined. When the weight-loss rate of smoldering is plotted against the oxygen concentration, a diagram such as that in Fig. 10 is obtained. By approximation to zero rate it is possible that the limiting oxygen value of smoldering propagation (LOI$_s$) may be calculated from this diagram.

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Zusammenfassung — TG, DTG und simultane DTA wurden zur Verfolgung der thermischen Zersetzungsprozesse von Zellulose in Stickstoff oder in einer oxidativen Atmosphäre eingesetzt. Während der Zersetzung entstandene flüchtige Produkte und feste Rückstände wurden analysiert um weitere Informationen zur Klärung der Kurven zu erhalten. Ein Hinweis auf mögliche flammende oder glühende Verbrennungen wird diskutiert. Die maximale Geschwindigkeit des Gewichtsverlusts, die prozentuale Menge des Rückstandes bei der Endtemperatur und die exothermen Peakflächen (DTA) könnten als geeignete Kriterien für die Entflammbarkeit der Zellulosen und die Aktivität der feuerhemmenden Substanzen betrachtet werden. Die aus den thermogravimetrischen Messungen errechneten formalen kinetischen

Parameter entsprechen den LOI (limiting oxygen index) Werten. Neue Beobachtungen wurden unter Einsatz einer Kombination der Thermoanalyse und der LOI-Techniken gemacht. LOI-Glut oder LOI-Entflammen werden mathematisch aus dem Zusammenhang zwischen der Geschwindigkeit des Gewichtsverlusts und der Sauerstoffkonzentration bestimmt.

Резюме — ТГ, ДТГ и совмещенный метод ДТА были использованы для контроля процессов термического разложения целлюлозы в атмосфере азота и в окислительной атмосфере. Летучие продукты и остатки, образуюшиеся во время разложения, были проанализированы для получения дополнительной информации для объяснения термических кривых. Обсуждено указание о возможном воспламенении тлении целлюлозы. Скорость макимальной потери веса, процентное количество твердого остатка, образующегося при конечной температуре разложения, и поверхности экзотермических пиков (ДТА), могут считаться тодходящими критериями воспламенимости целлюлоз и активности замедлителей пламени. Формальные кинетические параметры процесса вычислены из термогравиметрических измерений, соответственно значениям ЛОИ. Отмечены новые наблюдения при испольвании совмещенного термического анализа и метода ЛОИ. ЛОИ — тление и ЛОИ — воспламенение определяются математически из горафика в координатах скорость потери веса и концентрация кислорода.