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# THERMAL PROPERTIES OF FLAME RETARDANT VISCOSE FIBERS

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This paper discusses the problem of the thermal properties of flame retarding additives based on phosphazene derivatives and of the commercial agents Tomflam *B*, Flammex *T23P* and Stockhausen *W*-20949, as well as of flame resistant viscose fibers containing the above agents. Results of this investigation showed the action of Flammex *T23P*, Stockhausen *W*-20949 and phosphazene derivatives at lower temperature. Tomflam *B* acted within a much wider range of temperatures. The flame retardant additives applied to viscose fibers change the thermal properties of the fiber material.

The recent years have seen a fast development of studies on the theory of the combustion of polymers and the problem of flammability retardation [1–10]. The burning of polymers is a complex process, dependent on many factors. On heating, the polymer attains a temperature which is the initial temperature of pyrolysis. The pyrolysis mechanism and the rate of gas evolution have substantial effects on the flammability of polymers [1–6]. This process is of particular importance in the case of cellulose fibers, which are important raw material for textile fabrics and which belong to the group of fibers with the lowest resistance to the action of flame [5].

The process of combustion for cellulose runs in two stages:

- flaming combustion,
- glowing.

The flaming combustion always precedes the thermal decomposition of cellulose [1–6, 11–16]. Just over 140° [17] cellulose begins to decompose into volatile products, among others a carbon mono- and dioxide, methanol, ethane, ethylene, propane and other, liquid and solid substances with a low degree of polymerization [18–21]. Volatile products of pyrolysis and of the thermooxidizing decomposition, which are evolved as vapors and gases, find their way to the air surrounding the fiber material where, if the critical concentration is reached, ignition takes place. Most often, the charred residue left after the thermal decomposition glows and undergoes slow combustion in the solid phase.

The cause of ignition is the flammable low molecular weight substances evolved during the thermal decomposition process. The ease of material ignition depends on the nature of the vapors and gases being formed. With cellulose one observes a high yield of the volatile thermal decomposition products, reaching 80–90% [6]. The flame retardants used must influence the combustion process so as to produce substances which do not support the flame. In an extreme case these retardants direct the pyrolysis process in such a way that the decomposition of cellulose during the combustion results in the formation of the end-products, i.e. carbon, carbon dioxide and water, before the formation of flammable products [1–6].

A correct assessment of the usability of flame retardants requires a knowledge of their thermal properties. A method which allows one to establish the processes taking place in fibers on heating and burning, and also to foresee the effects of introduced flame retardants, is thermal analysis [2–6, 11, 22–26].

The aim of this work is to investigate the thermal properties of flame retardants, and of viscose fibers containing them.

## Experimental

Thermal investigations were carried out with flame retardants which had been obtained by methods developed at the Institute of Man-made Fibers, Technical University of Łódz, as well as with commercial products. Their properties are given in Tables 1 and 2. In investigations we also used viscose filaments (110 dtex) produced by the addition of the above retardants. The flame retardant viscose fibers were produced by the introduction of flame retardants to the viscose before spinning.

Thermal investigations were made with an OD-102 MOM derivatograph, using 100 mg samples of the investigated materials in an atmosphere of air in the temperature range 20–500° and at a heating rate of 10°/min.

## Results and discussion

Investigations into the thermal properties of flame retardants allow one to describe the processes which occur in them during heating, and also to estimate the quantity of the evolved decomposition products which suppress the flame.

Figure 1 shows the curves of the thermal changes which take place during heating of the flame retardants used and also the different thermogravimetric progress of these changes. Figure 2 presents the thermogravimetric masses lost by these compounds. On the basis of the results shown in the thermal curves, it may be stated that in the case of (2,3-dichloropropoxy)chlorophosphazenes one observes a relatively small endothermic effect, which precedes a distinct exothermic effect, as the result of thermal decomposition of this compound. The occurrence of the endothermic effect may be explained by the probable isomerization of chloroalkoxyphosphazene [24, 27]. A similar curve is obtained for (2,3-dichloropropoxy) (ethylenediamine)phosphazene; this derivative displays a higher decomposition temperature than that of the previous compound (Fig. 1, curves 1 and 3).

A different curve is observed for (2,3-dichloropropoxy)(*n*-butylamine)phosphazenes; the exothermic effect connected with the decomposition reaction occurs at a lower temperature than in the previous cases, with the maximum at 247°. The subsequent endothermic bands, with maxima in the range 280–283°, may be interpreted as processes which take place between the decomposition products of this compound (Fig. 1, curve 2).

In the case of Tomflame *B*, which is an organic phosphate containing a halogen, the exothermic effect interpreted as the decomposition of that compound takes place within the range 285–370°, with maximum at 350°. This effect is preceded by a small endothermic effect, with maximum at 245° (Fig. 1, curve 4).

The curve of Flammex *T23P* exhibits a broad band due to the endothermic effect within the range 115–290°. This effect is assigned to the process of homolytic detachment of the bromine radical from this compound [24]. The decomposition of this agent takes place within the range 290–324° (Fig. 1, curve 5).

The course of the thermal changes for Stockhausen W-20949 differs from those for the previously discussed compounds. The curve shows two consecutive exothermic effects, with maxima at 185° and 240°. The first effect can most probably be assigned to the transformation of the agent into polyphosporamide, and the second to the decomposition of this compound [16] (Fig. 1, curve 6).

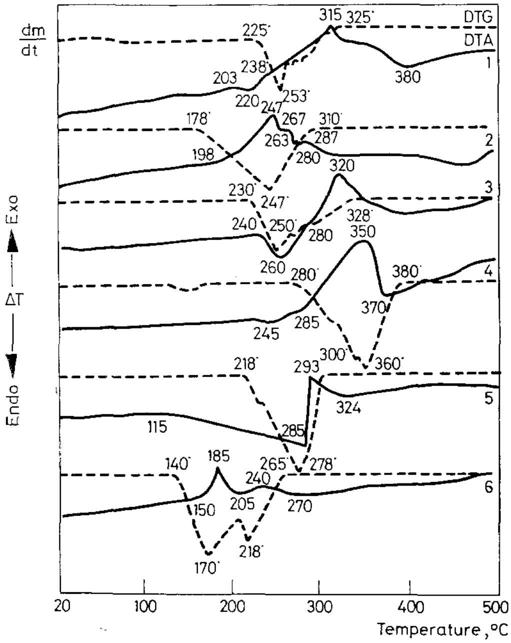

Fig. 1. DTA and DTG curves of flame retarding additives: 1. (2,3-dichloropropoxy)chlorophosphazenes; 2. (2,3-dichloropropoxy)(n-butylamino)phosphazenes; 3. (2,3-dichloropropoxy)(ethylenediamino)phosphazenes; 4. Tomflam *B*; 5. Flammex *T23P* 6. Stockhausen *W*-20949

Table 1

Physico-chemical properties of flame retardants based on the phosphazene derivatives

| Compound | Type of $NPCl_2$ oligomers used | Colour of liquid product | $n_D^{20}$ | Chemical composition, % | | | |
|---|---|---|---|---|---|---|---|
| | | | | C | H | P | N |
| (2,3-dichloropropoxy)chlorophosphazenes | mixture | light yellow | 1.5136 | 26.9 | 4.0 | 6.2 | 2.3 |
| (2,3-dichloropropoxy)(n-buthylamino)-phosphazenes | mixture | dark yellow | 1.5085 | 32.4 | 5.2 | 5.3 | 3.4 |
| (2,3-dichloropropoxy)(ethylene-diamino)phosphazenes | mixture | yellow | — | 33.3 | 5.0 | 4.4 | — |

Table 2

Physico-chemical properties of commercial flame retardants

| Name of flame retardant | Physical state | Colour | Density, $gcm^{-3}$ | Viscosity, 20 °C, cP | $n_D^{20}$ | Chemical composition, % | | | Producer |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | P | Br | N | |
| Tomflam *B* | liquid | light brown | 1.51 | 7 000 | 1.5810 | 4.8 | 40.0 | — | ZWCh "Chemitex-Wistom" Poland |
| Flammex *T23P* (2,3-dibromopropyl)phosphate | liquid | light yellow | 2.26 | 13 800 | 1.5765 | 4.4 | 68.4 | — | Berk Chem., Great Britain |
| Stockhausen *W*-20949 | liquid | dark brown | 1.66 | 24 000 | 1.5212 | 4.9 | 40.0 | + | Stockhausen A. G., GFR |

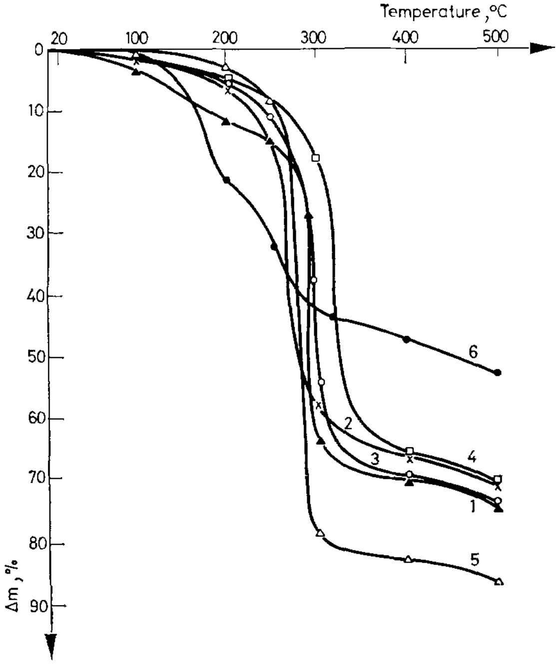

Fig. 2. TG curves of flame retarding additives: 1. (2,3-dichloropropoxy)chlorophosphazenes; 2. (2,3-dichloropropoxy)(n-butylamino)phosphazenes; 3. (2,3-dichloropropoxy)(ethylenediamino)phosphazenes; 4. Tomflam *B*; 5. Flammex *T23P*; 6. Stockhausen *W*-20949

One of the most important characteristics of flame retardants for viscose fibers is their decomposition at a temperature lower than/or close to the temperature of decomposition of the fiber material, i.e. within the range 330 – 400°. All the investigated compounds had decomposition temperatures lower than/or close to the value characteristic for regenerated cellulose. This observation allows the conclusion that the compounds used as additives will be effective flame retardants for viscose fibers.

It is important to know the mass losses of the investigated agents, which indicate the amounts of volatile products evolved on thermal decomposition. Data on this subject have been obtained by thermogravimetric analysis (Fig. 2). Tomflam *B* exhibited the greatest loss of mass within the range of decomposition temperatures for cellulose. Within a lower range of temperatures one observes a maximum loss of mass for the remaining agents.

The thermal investigations performed suggest the effectiveness of the agents as flame retarding additives for viscose fibers.

To determine the changes occurring during heating of the viscose fibers produced, their thermal properties were examined. The results are illustrated in Figs 3, 4 and 5.

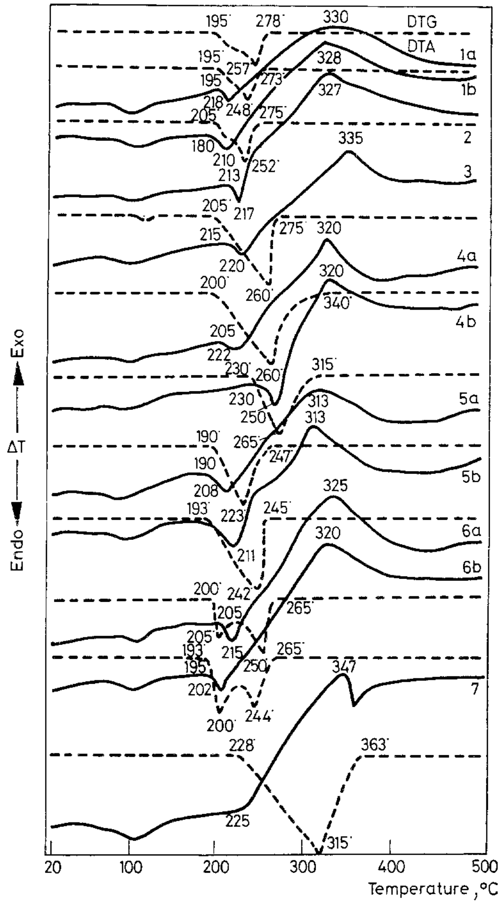

Fig. 3. DTA and DTG curves of viscose fibers containing: 1. (2,3-dichloropropoxy)chlorophosphazenes in a proportion of (in relation to the mass of cellulose): a) 8.4%; b) 14.5% 2. (2,3-dichloropropoxy)(n-butylamino)phosphazenes in a proportion of 14.0% in relation to the mass of cellulose; 3. (2,3-dichloropropoxy)(ethylenediamino)phosphazenes in a proportion of 12.1% in relation to the mass of cellulose; 4. Tomflam *B* in a proportion of (in relation to the mass of cellulose): a) 9.6%; b) 12.4%; 5. Flammex *T23P* in a proportion of (in relation to the mass of cellulose): a) 9.6%; b) 11.8%. 6. Stockhausen *W*-20949 in a proportion of (in relation to the mass of cellulose): a) 8.7%; b) 11.8%. 7. Without additives (standard fibers)

In the case of viscose fibers with additives, an endothermic effect precedes the exothermic one. The endothermic effect does not occur with the standard fibers. This phenomenon may be assigned to the reaction taking place between the phosphazene derivatives and cellulose. The products of this reaction decompose with an exothermic effect to yield non-flammable gaseous substances which extinguish the flame. A similar phenomenon is observed for viscose fibers which

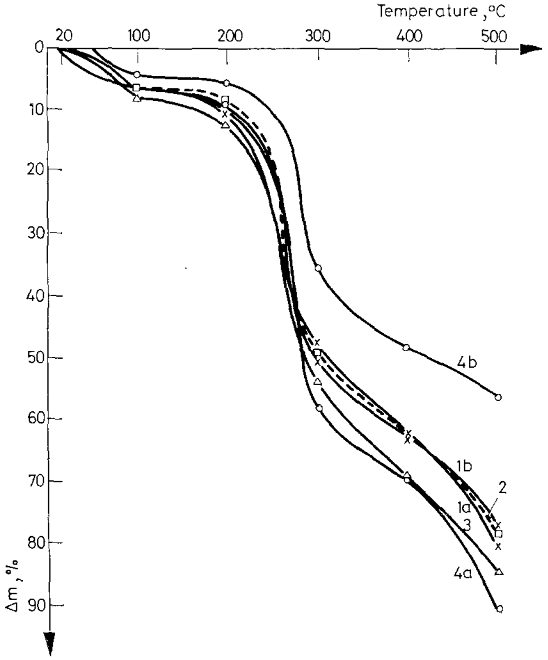

Fig. 4. TG curves of viscose fibers containing: 1. (2,3-dichloropropoxy-chlorophosphazenes in a proportion (in relation to the mass of cellulose): a) 8.4%; b) 14.5%. 2. (2,3-dichloropropoxy)(n-butylamino-phosphazenes in a proportion of 14.0% in relation to the mass of cellulose; 3. (2,3-dichloropropoxy)(ethylenediamino)phosphazenes in a proportion of 12.1% in relation to the mass of cellulose; 4. Tomflam *B* in a proportion of (in relation to the mass of cellulose): a) 9.6%; b) 12.4%

contain Tomflam *B* and Flammex *T23P*, where the endothermic effect is a result of the reaction of these compounds with cellulose, with simultaneous homolytic detachment of halogen radicals. The assumptions regarding the processes of flameproofing of viscose fibers with these agents are in agreement with the literature [15, 24].

Viscose fibers which contain an agent of the type of Stockhausen *W*-20949 are also characterized by an endothermic effect on heating, which may be interpreted as the reaction of cellulose with phosphoramide with the subsequent decomposition of the compound formed [29]. The maximum of the endothermic effect varies, depending on the quantity and type of the agent added to the fiber (Fig. 3). This effect occurs at the following temperatures for the following additives: phosphazene derivatives, 210–220°; Tomflam *B*, 222–250°; Flammex *T23P*, 208–211°; Stockhausen *W*-20949, 202–215°. The increase of the phosphazene or Stockhausen W–20949 content of the fibers lowers the temperature of the maximum rate of mass loss and the temperatures of the maxima of the endothermic and exothermic effects (Figs 4 and 5). In the case of viscose fibers containing Tomflam *B* and Flammex

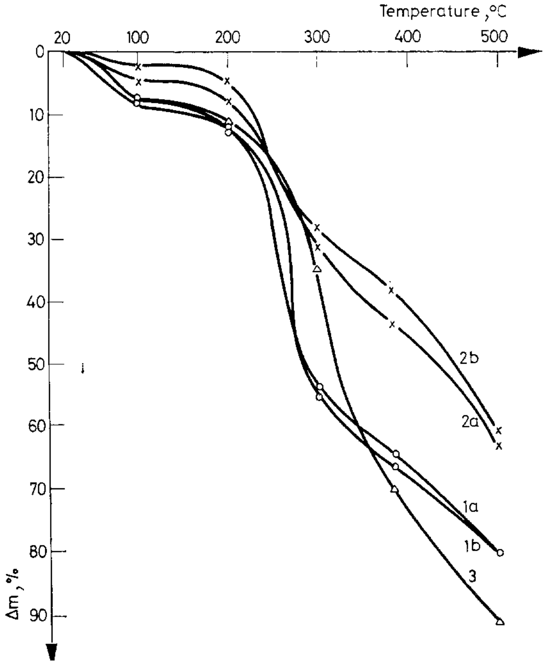

Fig. 5. TG curves of viscose fibers containing: 1. Flammex *T23P* in a proportion of (in relation to the mass of cellulose): a) 9.6%; b) 11.8%. 2. Stockhausen *W*-20949 in a proportion of (in relation to the mass of cellulose): a) 8.7%; b) 11.8%. 3. Without additives (standard fibers)

*T23P*, it is observed that the increase of quantities in the fibers causes an increase of the temperature of maximum mass loss and the temperature of the endothermic effect. This is most probably connected with the different courses of the thermal processes of the fibers and the courses of the corresponding processes under the influence of these agents. The flame retardants investigated in the viscose fibers cause a decrease of the temperature of the maximum endothermic effect, as evidence of the decomposition of the fiber material, and a decrease of the temperature of the maximum mass loss rate in comparison to the standard fibers.

The introduction of the agents into viscose fibers increased the residue remaining at 500° from 9% for standard fibers to ca. 20% for fibers containing phosphazene derivatives and Flammex *T23P* and to ca. 40% for fibers with Stockhausen *W*-20949 and Tomflam *B* (Figs 4 and 5). This phenomenon results from the action of the flame retardants used, which control the thermal decomposition so as to produce non-flammable substances.

Based on the thermal investigations on the viscose fibers, it may be stated that such flame retardants as Flammex *T23P*, Stockhausen *W*-20949 and phosphazene derivatives act at lower temperatures. Tomflam *B* acts within a much wider range of temperatures and is of undoubted merit in comparison with the agents discussed previously.

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Résumé — Le présent article étudie le problème des propriétés thermiques des additifs à base de dérivés du phosphazène retardant l'inflammation et d'agents commerciaux, comme Tomflam *B*, Flammex *T23P* et Stockhausen *W*-20949, ainsi que des fibres de viscose qui résistent à l'inflammation et contiennent ces agents. Les résultats de l'étude montrent que Flammex *T23P*, Stockhausen *W*-20949 et les dérivés du phosphazène agissent à température plus basse. Par contre, Tomflam *B* est actif dans un plus large intervalle de températures. Les additifs retardant l'inflammation utilisés dans les fibres de viscose modifient les propriétés thermiques du matériel fibreux.

Zusammenfassung — Es wird das Problem der thermischen Eigenschaften von auf Phosphazinderivaten beruhenden Zündverzögerungsadditivs und handelsüblichen Wirkstoffen wie Tomflam *B*, Flammex *T23P* und Stockhausen *W*-20949, sowie obige Wirkstoffe enthaltende flammensichere Viskosefasern behandelt. Die Ergebnisse zeigten die Wirkung von Flammex *T23P*, Stockhausen *W*-20949 und Phosphazinderivaten bei niedrigeren Temperaturen. Hingegen war Tomflam *B* in einem viel weiteren Temperaturbereich wirksam. Die in Viskosefasern angewandten zündverzögernden Additive änderten die thermischen Eigenschaften des Fasermaterials.

Резюме — В статье обсуждена проблема термических свойств добавок замедителей пламени, на основе производных фосфазена и таких продажных препаратов, как Томфлэм *Б*, Флэммекс *Т23П* и Штокхаузен *В*-20949. Наряду с этим исследована огнестойкость вискозных волокон, содержащих вышеуказанные добавки. Результаты исследования показали определенный эффект действия Флэммекса *Т23П*, Штокхаузера *В*-20949 и производных фосфазена при более низкой температуре. В тоже время Томфлэм *Б* оказывал действие в наиболее широком интервале температур. Замедлители пламени, введенные в вискозные волокна, изменяли их термические свойства.