

INVESTIGATIONS ON THE FLAME-RETARDATION OF CELLULOSIC FIBROUS MATERIALS

II. INVESTIGATION OF THE DEHYDRATION PROCESS

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The flame-retardation of Pyrovatex CP on cellulose substrate has been studied. Since levoglycosan, responsible for the flammability of cellulose, is formed in the main decomposition process by dehydration, the amounts of water vapour released from untreated and treated cellulose during this process were measured. The water contents of the decomposition products obtained in thermal measurements were absorbed in dioxan and determined dielectrometrically.

The results show that the water content of the decomposition products of untreated cellulose is much higher than that of treated cellulose. A reaction mechanism is suggested.

The mechanism of action of phosphorus-containing flame-retardants is still an open question, the solution of which is difficult, among others because these compounds are marketed with different compositions. Inorganic phosphates were first applied as fire-retardants, but organic phosphates have recently become widespread, mostly in the form of phosphorus amides and halogenated phosphorus esters. It has been found [1] that there is a synergetic effect if phosphorus and nitrogen or phosphorus and halogen are applied in combination.

Among flame-retardants containing phosphorus alone, a unique example is triphenyl phosphonate, investigated by Bostic et al. [2]. This compound has been found to exert its effect in the gas phase only, through a free-radical mechanism similar to that of hydrogen bromide.

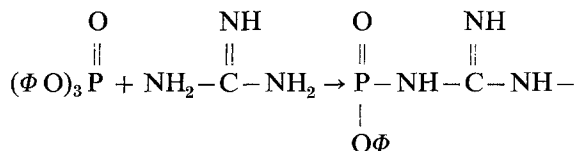
For triphenyl phosphite, it was assumed by Arney and Kuryla [3] that non-volatile additives exert their effects by inhibiting the formation of levoglycosan, i.e. suppressing the dehydration step. This takes place through a phosphorylation reaction at the most reactive carbon atom of cellulose, C₆. Phosphorylation may proceed more easily with aryl derivatives than with the corresponding alkyl compounds, since the latter are more liable to elimination scission of the C–O bond, and the resulting oxyphosphoric acid has a catalytic effect on dehydration, i.e. on the formation of levoglycosan.

The effects of phosphorus and nitrogen are superimposed when THPOH is applied in combination with ammonia, urea or guanidine, or when Pyrovatex CP (dimethyl phosphopropionic amide) is used. In their investigations of P and N-containing flame-retardants, Garn and Denson [4–6] subjected a mixture of cellulose and flame-retardant to pyrolysis, and identified the pyrolytic products

by parallel gas-chromatographic and mass-spectrometric measurements. It was assumed that the process starts with a reaction between acetic acid, resulting from the pyrolysis of cellulose, and ammonia, resulting from the pyrolysis of nitrogen bases, and finally acetonitrile is produced through the formation of ammonium acetate and acetamide. In a similar way, by dehydration in the gas phase, trimethylamine is formed from ammonia and methanol. Both processes are dehydration reactions catalyzed by phosphorus compounds in the solid phase.

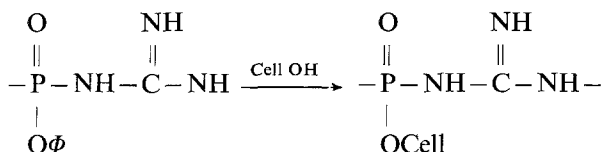
In a study on P and N-containing flame-retardants, the following models were applied by Hendrix and Drake [7, 8]: methyl- α -D-glycopyranoside, triphenyl phosphate + urea, triphenyl phosphate + guanidine carbonate. The suggested mechanism of flame-retardation is as follows.

Upon the action of heat, phosphorus amide is formed from triphenyl phosphite and guanidine:



This reaction may explain the synergetic effect between phosphorus and nitrogen.

The resulting compound reacts with cellulose:



The reaction takes place on OH group 6 of the cellulose, since the reactivities of the other OH groups are negligible in comparison. The flame-retardant additive suppresses the formation of levoglycosan in the solid phase. The formation of levoglycosan would assume the formation of an oxygen bond between carbons 1 and 6; this is inhibited, however, since OH group 6 is esterified by phosphorus amides formed upon thermal initiation from the phosphorus and nitrogen components. Consequently, these compounds inhibit levoglycosan formation through dehydration.

The various authors agree that the formation of cross-links plays an important role in the mechanism. As shown by Byrne [8], dehydrated cellulose forms a cross-link with the adjacent chain by aldol-type condensation, thereby reducing the probability of volatilization of smaller fragments, and thus increasing the amount of solid residue rich in carbon. Being polyfunctional, phosphorus compounds used as flame-retardants are also able to form cross-links.

Drews and Barker [9] analyzed the phosphorus and nitrogen contents of the tar-like final product obtained in the pyrolysis of cellulose. With Pyrovatex CP as treating agent, the total amount of phosphorus was found to remain in the solid

phase, regardless of the amount of phosphorus applied. It was concluded, therefore, that there is a direct interaction between the flame-retardant and cellulose during the flame-retarding process, but no chemical reaction occurs at all between the decomposition products of cellulose and the flame-retardant additive. It must be noted, however, that these results are not generally valid, and do not hold, for example, for $O=P-N(CH_3)_2$.

Our aim was to investigate the mechanism of flame-retardation processes by acquiring information experimentally on the nature of the gross chemical reaction. For this purpose, thermal analysis and other analytical methods were used. Considering the literature data discussed, it can be assumed that the gross flame-retarding chemical process must be dehydration. It is not completely clear, however, whether the catalysis or the inhibition of this dehydration leads to a better anti-inflammation effect.

Experimental

Apparatus and materials

The complex thermoanalytical investigation was carried out with a MOM derivatograph. The dielectrometric water determination was performed with a precision dielectrometer of type OH-302. Infrared spectra were recorded on a Zeiss UR-10 infrared spectrophotometer.

The measurements were carried out under the following experimental conditions. Sample weight: 100 mg, ceramic crucible, empty reference crucible, heating rate: ca. $5^\circ/\text{min}$, static air atmosphere.

The thermoanalytical curves of untreated and treated (Pyrovatex CP) cotton have already been published [10]. As regards the determination of water, the following information can be obtained from the curve. With both the untreated and the treated samples, the desorption of ca. 5% of adsorbed moisture is terminated by ca. 120° . According to the literature [11], the formation of levoglycosan, i.e. the dehydration process, occurs in the main decomposition of cellulose. It is therefore necessary to determine the temperatures at which the main decomposition of untreated and treated samples is completed. This was found to be 375° for untreated, and 310° for treated cellulose (cotton).

The amount of water formed in the main decomposition process was determined quantitatively in an apparatus consisting of two parts, one for absorbing the gas products of the decomposition and one for measuring water content.

Water content was determined by a simple, fast and accurate method, dielectrometry, in which the change in water content is monitored by measuring the dielectric constant of the medium. The amount of water was determined after absorption in dioxan. In all cases samples of ca. 1 g and heating rates of ca. $5^\circ/\text{min}$ were applied. Under these conditions a well-measurable amount of water leaves the system. Above the specimen holder and the reference crucible a titration accessory

was mounted [12], through which the gas may enter and leave the system. Carrier gas (air) was dried in a column filled with silica gel, and its flow rate was measured with a rotameter. The gases leaving the derivatograph were absorbed in two gas-washing bottles. According to the results, no water vapour entered the second bottle; this was used only to remove other decomposition products which might damage the pump. The rate of suction was also controlled by a rotameter. As the thermal decomposition was preceded by the removal of adsorbed moisture, which

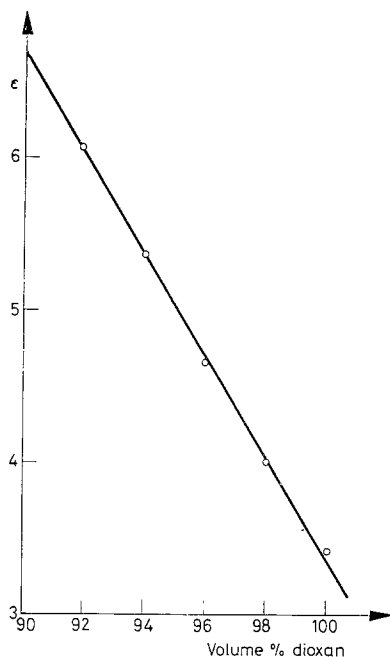


Fig. 1. Calibration curve for determination of water content by means of dielectrometric method

Table 1

Sample	Weight, mg	Dielectric constant	Water, v %	Water, re-leased from 1.5 g sample, v %	Difference, v %
Treated	1201.2	3.55	0.7	0.9	
Untreated	1002.3	4.32	2.9	4.4	3.5
Treated	1173.0	3.62	0.8	1.0	
Untreated	1441.9	4.73	4.1	4.3	3.3
Treated	1446.3	3.66	0.9	0.9	
Untreated	1306.1	4.68	4.0	4.4	3.5
Average					3.4

was not to be measured here, this amount of water was collected in a separate bottle.

The calibration curve used for the measurements is shown in Fig. 1.

The experimental results are given in Table 1.

Results

Dielectrometry has been found to be suitable for the quantitative determination of water produced in the pyrolysis of cellulose. Although the method does not allow the amount of water to be recorded continuously, it is fast, accurate and simple. It can be used to particular advantage when polar contaminating components are to be detected in non-polar solvents. If the dielectric constant of the non-polar solvent is sufficiently small ($\epsilon = 2$ to 5), a quantitative determination of water can also be accomplished.

There is also a possibility for the continuous recording of the amount of water vapour formed in the main decomposition process by applying a thermogastitrimetric accessory to the derivatograph. This method, however, is inapplicable for cellulose, since the aldehyde and ketone products arising from the pyrolysis of cellulose would form adducts with the Karl Fischer standard solution.

Our experimental results can be used to compare the amounts of water vapour arising from the thermal decompositions of untreated and treated cellulose samples under the same experimental conditions. It has been found unambiguously that the amount of water vapour decreases after treatment with Pyrovatex CP.

The percentage water contents of the gas products obtained in the thermal decompositions of untreated and treated cellulose can also be determined semi-quantitatively with the instrument. For this purpose an exactly known amount of water, also absorbed in dioxan, was measured in the apparatus dielectrometrically.

The different amounts of water were produced by the thermal decomposition of $\text{Ca}(\text{COO})_2 \cdot \text{H}_2\text{O}$. On the basis of the TG curves obtained and the calibration curve almost the total amount of water (average: 96%) could be detected by the dielectric method with small variance. Thus, the mean loss is altogether 4%.

These results permit one to estimate the percentage water contents of the decomposition products obtained in the main decomposition processes of untreated and treated cellulose.

From an average of 1500 mg untreated sample, 4.3 w% of water was measured in 10 ml dioxan. This quantity corresponds about 30% water of the original sample.

From an average of 1500 mg sample treated with Pyrovates CP, 0.9 w% of water was measured in 10 ml dioxan. This is about $\approx 6\%$ water of the original sample.

It should be noted that there is no need to use anhydrous dioxan for the measurements, since the system cannot be isolated completely from atmospheric moisture.

The low water content of dioxan, however, introduces no error into the results, since it is eliminated with the use of the calibration curve.

As a conclusion, it can be stated that treatment with Pyrovatex CP effects the thermal decomposition of cellulose by decreasing the amount of water vapour formed in the main decomposition, presumably by inhibiting the dehydration process. Since levoglycosan is a product of this process, the above result supports the inhibition theory, according to which Pyrovatex CP inhibits the formation of the flammable intermediate in the solid phase.

Infrared spectroscopic investigations

The infrared spectra also indicate that one of the products of the thermal decomposition of cellulose is levoglycosan, and upon treatment with flame-retardants the amounts of oxidized products decrease.

The infrared spectrum of the solid residue obtained under the thermal decomposition of cellulose was recorded and compared with the spectra of the solid residues remaining in the course of the main decomposition processes of untreated and treated cellulose samples.

In the spectrum of the solid residue obtained in the course of the main decomposition of cellulose treated with THPC + urea + Na₂HPO₄, the carbonyl and condensed aromatic bands appear with lower intensities. From the decreased intensity of the OH bands between 1300 and 1450 cm⁻¹, it can be concluded that the amount of levoglycosan is also smaller here.

As can be seen from the above, the infrared spectra support the results obtained with the thermal and dielectrometric methods.

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RÉSUMÉ — On a étudié l'effet ignifuge du Pyrovatex CP sur un substrat cellulosique. Etant donné que la lévogylosane, responsable de l'inflammabilité de la cellulose, se forme par déshydratation, lors du processus principal de décomposition, on a mesuré respectivement les taux de vapeur d'eau dégagés respectivement par les celluloses traitées et non-traitées pendant ce processus. L'eau contenue dans les produits de décomposition obtenus lors des mesures thermiques a été absorbée dans le dioxane puis dosée par une méthode diélectrométrique.

Les résultats montrent que la teneur en eau des produits de décomposition de la cellulose non-traitée est beaucoup plus élevée que celle de la cellulose traitée. Un mécanisme réactionnel est proposé à partir de ces résultats.

ZUSAMMENFASSUNG — Die flammenhemmende Imprägnierung von Pyrovatex CP wurde an einem Zellulosesubstrat untersucht. Da das für die Entflammbarkeit der Zellulose verantwortliche Levogylosan sich in dem Hauptzersetzungs Vorgang durch Dehydratisierung bildet, wurde die im Laufe dieses Vorganges aus unbehandelter und behandelter Zellulose freigesetzte Wasserdampfmenge gemessen. Der bei den thermischen Messungen erhaltene Wassergehalt der Zersetzungsprodukte wurde in Dioxan absorbiert und durch eine dielektrometrische Methode bestimmt.

Die Ergebnisse zeigten, daß der Wassergehalt der Zersetzungsprodukte der unbehandelten Zellulose viel höher ist als jener der behandelten Zellulose. Aufgrund der Ergebnisse wird ein Reaktionsmechanismus vorgeschlagen.

Резюме — Изучено действие Пироватекса CP на образце целлюлозы, как замедлителя пламени. Поскольку левовращающийся гликозан, образующийся в процессе разложения при дегидратации, является ответственным за воспламеняемость целлюлозы, было измерено количество выделяемого водяного пара во время этого процесса из необработанной и обработанной целлюлозы. Вода в продуктах разложения, полученных при термических измерениях, была абсорбирована диоксаном и содержание ее было определено диэлектрометрическим методом. Результаты измерений показали, что содержание воды в продуктах разложения необработанной целлюлозы намного выше, чем в обработанной. На основе результатов предложен механизм реакции.