

Investigations of the Action of Flame Retardants in Cellulose. II: Investigation of the Flame-Retardant Action of Polyphosphonitride in Cellulose

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Synopsis

Pure regenerated cellulose fibers and those containing various amounts of phosphorus nitride were pyrolyzed under different conditions in the temperature range of 150–440°C. Easily volatile liquid pyrolysis products, the tar fraction of limited volatility, and the charred residue were determined gravimetrically. The liquid volatiles were analyzed by combined gas chromatography/mass spectrometry for their water content. The tar fraction and the charred residue were inspected by infrared (IR) spectroscopy. The studies revealed that the phosphorus nitride flame retardant enhances the onset of the pyrolytic decomposition and the release of water at substantially lower temperatures as observed for pure cellulose. The water release favors the carbonization and its extent reduces the formation of levoglucosan as a precursor of easily flammable pyrolysis products. Thus phosphorous nitride must be classified into the water release favoring flame retardants.

INTRODUCTION

In a recent publication in this Journal,¹ we have presented the results of a study on the flame-retardant action of an organic pyrophosphate compound carrying a thionophosphoryl group (2,2'-oxybis-(5,5-dimethyl-1,3,2-dioxaphosphorinane-2,2'-disulfide, i.e., Sandoflam 5060[®]) for cellulose substrates. In this study thermal volatilization analysis (TVA) technique was used to investigate the thermal decomposition of cellulose substrates without and in the presence of the flame retardant. The highly volatile products, the tar fraction of limited volatility, and the charred residue were characterized using gas chromatography, mass spectroscopy and infrared (IR) spectroscopy.

The study revealed that the incorporation of the flame retardant enhanced the water release from the cellulose and shifted its thermal decomposition to remarkably lower temperatures. The enhanced water release hinders the thermal feedback and suppresses the formation of levoglucosan which is regarded as the precursor of flammable pyrolysis products.

Another very interesting group of compounds which should have flame-retardant action in combination with cellulose substrates are the phosphorus nitrides, such as P_3N_5 , P_2N_3 , and $(PN)_x$. In these compounds nitrogen and phosphorus are contained in mol ratios of 0.75 to 0.45. It is known that the simultaneous presence of phosphorus and nitrogen exerts a synergistic effect,

enhancing quite often the flame-retarding action of phosphorus compounds in such a way that a satisfactory effect is achieved at lower levels of phosphorus content.² The phosphorus nitrides are polymeric amorphous compounds of reasonably good stability against water and aqueous alkaline or acid solutions and with high melting points. When vaporized the vapor contains PN molecules.

They are manufactured by reacting phosphorus chlorides with ammonia. In this reaction Phospham $(\text{NPNH})_n$ is formed as an intermediate. On heating to 500°C, this intermediate is first transformed to P_3N_5 and in further heating to higher temperatures it goes over to $(\text{PN})_x$.

The favorable simultaneous presence of phosphorus and nitrogen in phosphorus nitrides and the good stability toward alkali and acids caused the Austrian viscose rayon fiber producer Lenzing Aktiengesellschaft to enter into a cooperative effort with Knappsack Aktiengesellschaft (a fully owned subsidiary of Hoechst A.G.) as a potential producer of phosphorus compounds.³ It is in this connection quite interesting to note that phosphorus nitrides when fully transformed to $(\text{PN})_x$ are according to the results of DTA investigations quite stable to temperatures well beyond 600°C. In DTG measurements, however, they show a slight but continuous loss of weight even before this temperature range indicating vaporization. Since the joint work soon revealed success in the incorporation of phosphorus nitrides via the viscose process into regenerated cellulose fibers resulting in satisfactory flame-retardant effect, it can be assumed that on heating phosphorus nitride reacts with the cellulose substrate under dehydration of the cellulose. On the other hand, DTA studies on cellulose fibers and films containing phosphorus nitride revealed that apparently its action follows a mechanism somewhat different to the one followed by other flame retardants. It also causes the thermal decomposition to occur at approximately 290°C instead of about 340–350°C without flame-retardant additive. However, its action is accompanied by a strong endothermic rather than exothermic reaction. Many other phosphorus-containing flame retardants, such as the phosphorinane sulfide compounds on which we reported recently, initiate an exothermic cellulose decomposition.⁴

From these observations it seemed interesting to us to study the action of phosphorus nitrides as a flame retardant for cellulose more thoroughly, applying the techniques used in our recently published study.

EXPERIMENTAL

Since the experimental details have been discussed thoroughly in the previous publication,¹ they are presented here only briefly.

Pure high wet modulus viscous fibers and those with different amounts of incorporated polyphosphonitride were obtained from Lenzing AG. The flame-retardant additive had been incorporated into the viscose rayon fibers by adding it as a fine powder (approx. 1 to 3 μm particle size) to the viscose-spinning dope prior to the fiber spinning.

The isothermal pyrolysis studies were performed in a TVA apparatus (Thermal Volatilization Analysis)⁵ under reduced pressure (1000 Pa) and in high vacuum (ca. 10 Pa) at different temperatures in the range of 150–450°C. The liquid products evolved during the pyrolysis treatment were condensed

for inspection in a cold trap. In addition, it was differentiated between the "charred residue" remaining in the pyrolysis vessel and a minor volatile "cold ring fraction," which was deposited during the heat treatment just behind the hot zone of the pyrolysis vessel as tar.

The amount of water in the liquid fraction was determined by gas chromatography coupled with mass spectroscopy. The mass spectrometer was applied as selective detector for the molecule ion of water ($m/e = 18$).

The char and the tar fraction were inspected by means of infrared spectroscopy, mainly with respect to the OH vibration at 3450 cm^{-1} . For comparable results exactly 10 mg of the samples were mixed with 3 g of KBr and 150 mg of the mixture were pressed into a pellet.

RESULTS

Yields of char, tar, and volatiles during isothermal pyrolysis of fiber samples containing varying amounts of flame-retardant polyphosphonitride. After isothermal pyrolysis at 1000 Pa residual air pressure at temperatures ranging from 150 to 450°C , the amounts of dry char and of volatile liquids were determined gravimetrically. From the data obtained the amounts of tar and other volatiles (gases,⁶ CO, CO₂) were calculated. The results are summarized in Figure 1.

The data in Figure 1(a) show that the addition of polyphosphonitrides to the cellulose results in an onset of the thermal decomposition reaction at approximately 200°C whereas pure cellulose starts to decompose only at around 280°C . At higher temperatures, the amount of residual char remains, with approximately 40% constant for both cellulose fibers containing 12 or 22% flame retardant, respectively. For the case of the pure cellulose without flame-retardant additive the amount of char left shows a marked falling tendency with increasing pyrolysis temperature.

Figure 1(b) shows the changes in % tar with increasing pyrolysis temperature. It can be easily seen that the formation of tar (cold ring fraction) is remarkably suppressed by the presence of the polyphosphonitride flame retardant in the cellulose substrate.

Inspection of the data given in Figure 1(c) shows that the release of liquid volatiles from the thermally treated celluloses occurs at remarkably lower temperatures for the cellulose samples containing the flame-retardant additive, specifically between 200 and 250°C . The cellulose sample containing no flame retardant, however, shows the release of liquid volatiles only at temperatures between 250 and 350°C .

To investigate the influence of the residual air pressure, similar experiments were performed at 260°C in a vacuum of 10 Pa. The results are listed in Table I.

Comparison of these results with those obtained in the 260°C pyrolysis at the higher residual air pressure of 1000 Pa reveals little difference. Only the sample with 22% phosphorus nitride shows a somewhat reduced yield of liquid decomposition products at lower pressure, while the cold ring tar fraction is correspondingly increased.

Determination of the water release during isothermal pyrolysis (at 1000 Pa). In Figure 2, the amounts of water (in g/cellulose in the samples)

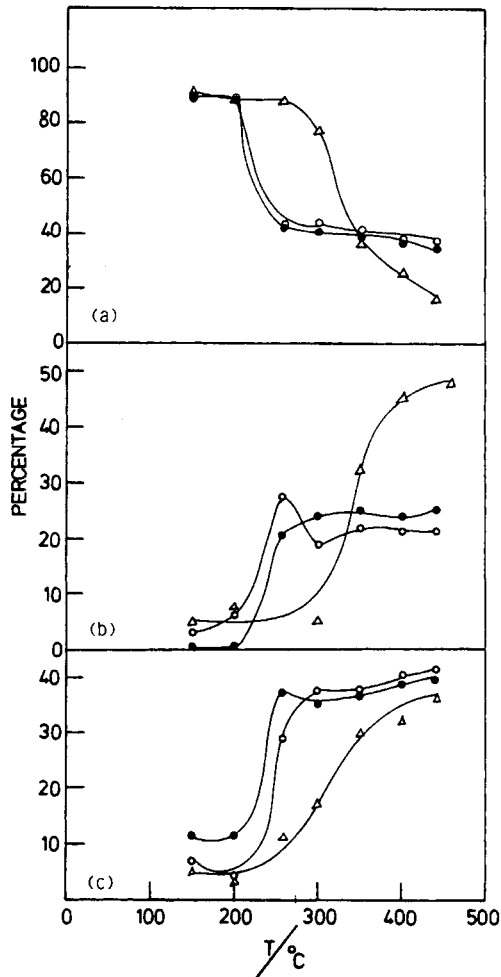


Fig. 1. Percentage of char (a), cold ring tar fraction (plus gaseous, not condensable pyrolysis products) (b), and condensable volatile liquid pyrolysis products (c) observed in the isothermal pyrolysis experiments at 10 Pa residual air pressure: (Δ) for pure cellulose, (\circ) for cellulose containing 12%, and (\bullet) 22% phosphorus nitride, respectively.

TABLE I
Isothermal Pyrolysis (at 10 Pa Residual Air Pressure, 260°C for 1 h)
of Cellulose Fibers Containing Various Amounts of Phosphorus Nitride

Weight % of PN in fiber	Total weight loss %	Char %	Cold ring tar fraction ^a %	Liquid volatiles %
0	13	87	1	12
12	56	44	27	30
22	58	41	31	28

^a Includes gaseous volatiles.

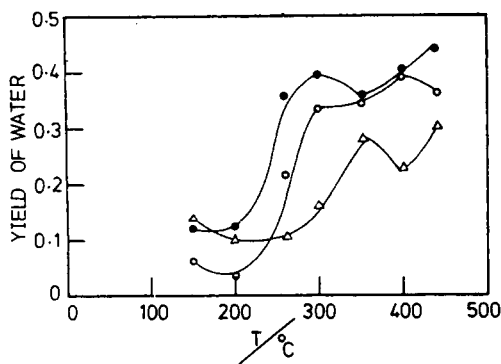


Fig. 2. Yields of water released in isothermal pyrolysis experiments at 260°C and 1000 Pa residual air pressure as determined by combined gas chromatography/mass spectrometry: (Δ) for pure cellulose, (\circ) for cellulose containing 12%, and (\bullet) 22% phosphorus nitride, respectively.

contained in the volatile fraction determined by combined gas chromatography/mass spectrometry are plotted against the pyrolysis temperatures. For the cellulose specimen containing 12 and 22% flame-retardant additive, respectively, water is released in substantial amounts and with a high rate at pyrolysis temperatures between 200 and 300°C. On the other hand, in the case of pure cellulose, the water release does not start before 250°C and does not reach as high values as observed for the flame-retardant containing samples.

A comparison of Figure 2 (water released) with Figure 1(c) (total liquid volatiles released) shows that the major portion of the liquid pyrolysis products is water.

Infrared studies on the charred residues and cold ring tar fractions.

In accordance to the enhanced water release, the charred residues and their tar fractions show increased transmission of IR radiation at 3450 cm^{-1} , associated with the OH vibration, indicating also enhanced dehydration, as can be seen from the data in Table II. The data also demonstrate the completion of the loss in hydroxyl functions for samples containing flame retardant at pyrolysis temperatures lower than 260°C.

TABLE II
Quantitative IR Studies on Charred and Cold Ring Tar Fractions from Isothermal Pyrolysis Experiments (at 10 Pa for 1 h) on Cellulose Fiber Samples Containing Various Amounts of Phosphorus Nitrides

Weight % of PN in fiber	Char/tar	Pyrolysis temperature °C	Transmission at 3450 cm^{-1} in %
0	untreated	—	12
0	char	260	55
0	char	400	88
22	untreated	—	32
22	char	260	73
22	char	400	71
22	tar	400	73

CONCLUSION

The results of our study reveal that phosphorus nitride acts in the course of pyrolysis as a dehydration agent for the cellulose. It reduces remarkably the temperature at which cellulose decomposition starts. It is interesting to note that in this respect it acts in the same way as the organic pyrophosphate flame retardant investigated by us earlier,¹ even though both compounds differ completely in their chemical structure.

From studies of the flame-retardant action of organic phosphorus compounds in contact with cotton textiles it is long since known that they act, in contrast to halogen compounds, in the solid phase. On heating, the organic phosphorus compound decomposes under formation of polyphosphoric acid, which extracts water from the pyrolyzing cellulosic substrate thus carbonizing it.^{7,8} The mechanism of the dehydration and subsequent carbonization will be either etherification or acid-catalyzed water elimination leading through unsaturated states to carbon formation. This prevents the formation of easily combustible intermediates. Esterification of glucose base units at C(6) will probably reduce the formation of levoglucosan,⁸ which in the absence of a flame retardant is the key intermediate in cellulose pyrolysis. In the case of phosphorus nitrides, we assume that their vapors, formed even at relatively low temperatures, will react with water split off from the pyrolyzing cellulose, forming phosphorous acids and ammonia. They, being in situ with the cellulose substrate, exert their flame-retardant action possibly involving the beneficial effect known for nitrogen-phosphorus combinations.⁹ An indication for this type of action is our finding that in the presence of phosphorus nitride the abstraction of water from cellulose is also higher than 1 mol/glucose unit, thus interfering with levoglucosan formation. The flame-retardant action of phosphorus nitride in combination with cellulose is thus due to: (a) the enhanced splitting of water at remarkably lower temperatures than in the case of pure cellulose, and (b) the abstraction of more than 1 mol of water per glucose unit reducing the formation of easily flammable pyrolysis products via levoglucosan.

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