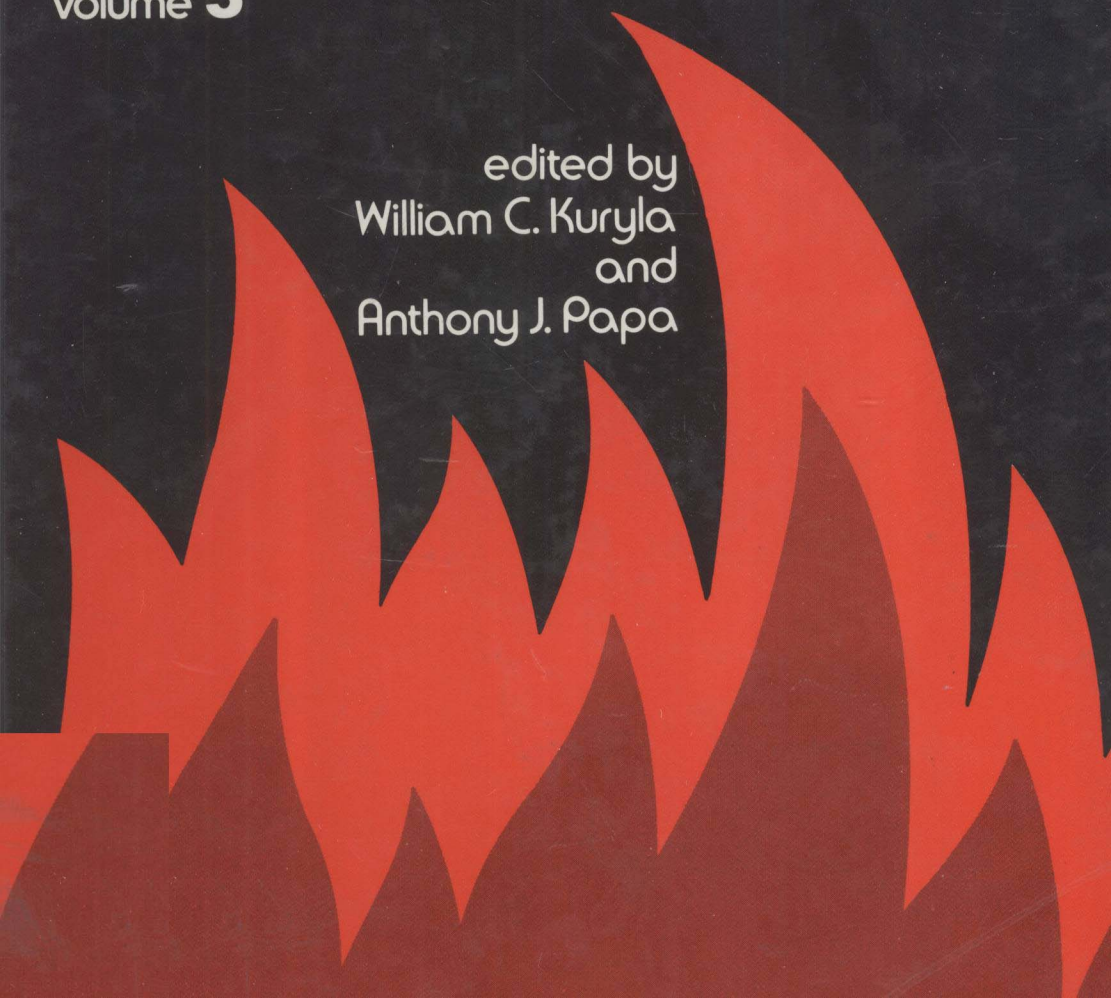


# Flame Retardancy of Polymeric Materials

volume **5**

edited by  
William C. Kuryla  
and  
Anthony J. Papa



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# Flame Retardancy of Polymeric Materials

Volume 5

*Edited by*

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South Charleston, West Virginia*

MARCEL DEKKER, INC. New York and Basel

Library of Congress Cataloging in Publication Data (Revised)

Kuryla, William C.

Flame retardancy of polymeric materials.

Includes bibliographical references and indexes.

1. Fire resistant polymers. I. Papa, Anthony  
Joseph, joint author. II. Title.

TP1092.K87 620.1'92 72-90965

ISBN 0-8247-6778-0 (v. 5)

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MARCEL DEKKER, INC.

270 Madison Avenue, New York, New York 10016

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

## PREFACE

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Flame retardancy of textiles has been of long-standing importance to mankind — extending to the times of the Egyptians. With recent government emphasis on the fire hazards associated with flammable fabrics, the practical and theoretical significance of this field has gained tremendous priority. Consequently, this volume places emphasis on an integrated presentation of the fundamental mechanistic concepts and technological and application principles of flame-retarding textiles.

The volume begins with a presentation of the various mechanisms proposed for the degradation of cellulosic fabrics and discusses the scope and validity of the proposals. Chemical and physical modes of action of a variety of flame retardants on fabrics are presented (e.g., the use of fundamental colorimetric devices for measuring heat evolution). Effectiveness is exemplified primarily with commercial phosphorus-containing flame retardants, and the effects of reagent's features, such as valence state, electrophilicity, synergistic behavior, and the like, on cellulose flammability are discussed in detail.

In the second chapter, treatment of textile flame retardancy is extended to include theories and practices related to the increasingly important blends of cotton with polyesters. Such commercial blends of naturally occurring thermoset polymers with synthetic thermoplastic polymers have confronted the chemist with new challenges to flame retardancy. And this has developed into an area of tremendous importance. The specific chemical and physical problems, current combustion theories, and developing modes of flame retardancy are reviewed here.

The final chapter of this volume presents a concise survey of the use of red phosphorus in a broad variety of polymers. This chapter is a departure from the conventional approach of looking at flame-retardant reagents for a single polymeric system. This fresh approach should have appeal to research and application chemists working with different polymer systems. In addition to flammability data, possible mechanistic pathways of action in several polymer systems are presented for this unique reagent.

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# 1

## FLAME RETARDANCE OF COTTON AND OTHER NATURALLY OCCURRING CELLULOSIC POLYMERS

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### I. INTRODUCTION

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The flammability of cotton and other cellulosic materials has been recognized for many years, although there is still considerable disagreement concerning the magnitude of the hazard that they pose to the general public. This arises from the fact that flammability is a relative, rather than an absolute, matter. Even metals may burst into flame when exposed to extreme conditions. Thus there is no such thing as a truly "flameproof" fabric, and the best that can be attained is some given level of fire resistance. Fortunately, cellulose has a chemical composition which makes it particularly amenable to treatments which can render it resistant to both flaming and glowing combustion.

Application of flame retardants to cotton textiles began about 1640 when theater canvas was treated with clay and plaster of Paris. By 1740, alum was found to give textiles flame-resistant properties, as was ammonium phosphate by 1786. Gay Lussac completed the first systematic investigation of the use of flame retardants in 1820. From this work he concluded that the most effective salts were those which were either low melting and capable of covering the material with a glassy layer or those which would decompose into nonflammable vapors on heating [1]. Since Gay Lussac's investigation, extensive literature pertaining to flame retardants has become available. Unfortunately, much of this information is of more practical than theoretical value, and consequently, it is of little application to a description of fundamental mechanisms of pyrolytic degradation and flame retardation. In recent years, with the use of chromatographic and thermal analytical techniques to study the thermal decomposition, fundamental data have begun to be collected.

Flaming is a vapor-phase process which is predominantly cyclic in nature. In the initial stages of burning, heat is supplied to the non-volatile polymer substrate initiating an endothermic degradation reaction which is generally conceded to be predominately pyrolytic in nature. There seems to be little evidence of significant oxidative processes occurring in the condensed phase. The products of this polymer pyrolysis diffuse to the surface of the fabric and are released into the atmosphere directly above the fabric. It is at this point that these flammable gaseous products begin to mix with the oxygen of the air so that combustion can take place. This is an exothermic process, of course, and the heat thus liberated is partially transferred back to the fabric surface to continue the polymer pyrolysis, assuring a continuous supply of fuel for further flame propagation. This leads to the conclusion that the heat flux at the surface of the solid phase is one of the most critical factors in determining whether the material will exhibit self-extinguishing characteristics. Unfortunately, this is not an easy parameter to measure unambiguously; however, the heat flux should be related to the total heat liberated during the burning of a fabric. From this it follows that the efficiency of a flame-retardant treatment should correlate with its ability to reduce the heat evolution during combustion of a given quantity of substrate.

Glowing is a completely different process since it occurs in the solid phase and does not depend on any volatilization processes for its fuel supply. It is a relatively slow combustion and is usually not of great concern in cellulose except for very specific items such as carpets, upholstery, and mattresses, where the major safety hazards are associated with smoke and toxic gas generation rather than heat

evolution. The glowing of solid carbon is known to be enhanced by many metal oxides which exert a catalytic effect of the oxidation and result in lower ignition temperatures and increased burning rates [2]. Many of these same metal oxides and other metal salts appear to have a similar effect of the carbonaceous char remaining after cellulosic material has been subjected to a flame. On the other hand, both carbon and the cellulose can be protected from the glowing by the presence of certain elements such as phosphorus. These are thought to alter the course of the oxidation reactions to a less exothermic path, producing carbon monoxide instead of carbon dioxide. This would result in a decrease in the quantity of heat liberated by approximately 70 kcal/mol so that there would be insufficient heat to sustain the solid-phase combustion [2].

The vapor-phase flaming is considerably more complicated and also constitutes a more widely recognized hazard. In spite of being quite intensively studied for several decades, the nature of the flaming process and the mechanisms of flame-retardant action are not well defined. Historically, four mechanistic explanations pertaining to flame retardation received widespread acceptance by 1947 [3]. These were based on chemical, coating, gas, and thermal theories. According to chemical theories, the flame-retardant substance acts as a catalyst by promoting degradation of the substrate in a direction other than that taken by untreated cellulose. Strong alkali, mineral acids, and oxidizing agents are effective flame retardants for cellulose but degrade the fabric substrate. However some derivatives of these substances do not cause degradation and produce flame-retardant substances when decomposed at or near flaming temperatures. Substances which produce strong alkali at high temperatures include the alkali metal salts of weak acids. None of the neutral salts of strong acids and bases decompose to a large extent at flaming temperature; thus, to produce strong acids the acid salt of a weak base is preferred. Ammonium salts of strong acids are among those most easily decomposed. Magnesium and zinc chlorides have low thermal stability and usually exhibit pronounced flame-retardant properties. Easily reducible oxides have proven to be effective in both the hydroxide and hydrated forms [3].

The coating theory proposed by Gay Lussac is still widely used to explain the flame-retardant properties of low-melting inorganic salts. It is postulated that upon contact with a flame, a glassy film of fused salt is formed on the surface of the fabric. The film excludes oxygen from the system, thus preventing propagation of the combustion reaction. Compounds which melt with the evolution of gases to form stable foams also coat the substrate surface. The flame retardation

is accomplished by a mechanism similar to that of the low-melting salts.

Certain materials decompose at elevated temperatures yielding inert or difficultly oxidizable gases. Supporters of the gas theories hypothesize that application of such compounds to textile materials decreases flammability by either diluting the flammable gases produced during pyrolysis or by blanketing the substrate with an inert atmosphere. Thus, exposure of the substrate to an oxidizing atmosphere should be reduced or eliminated. Such changes in the fuel-to-air ratio are presumed to raise the ignition temperature of the substrate, thereby retarding flaming. However, if the quantity of inert gases produced by the retardant is compared with that of the gaseous products resulting from the thermal decomposition of cellulose, none of the known flame retardants produces inert gases in quantities substantially greater than those volatiles produced by cellulose [4]. Despite this fact, the theory was widely accepted [3].

Supporters of the thermal theories of flame-retardant mechanisms hypothesize that effective retardants should be capable of maintaining fabric temperatures below the minimum combustion temperature for cellulose. According to such theories, the retardant must be able to either dissipate large quantities of energy internally or possess an ability to conduct this energy away from the flame front at a rate comparable to or greater than that at which it is supplied. This seems implausible since numerous compounds undergo energy changes during pyrolysis that are comparable to those of known retardants but are completely ineffective. It has been shown by differential thermal analysis (DTA) that the number and magnitude of endothermic changes in no way correlate with the effectiveness of a compound in flame-retardant applications [3].

## II. EVALUATION AND CHARACTERIZATION OF FLAME-RETARDANT ACTION

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Although the current literature still contains periodic references to these four early mechanistic theories, most investigations now take a slightly different approach to the problem. Because of the cyclic nature of the flaming process, it is usually amenable to attack at any of several points. Effective flame retardants may, therefore, be considered to act in the condensed phase, the vapor phase above the decomposing polymer, or a combination of the two. Retardants which act in the gas phase exert their effect by functioning as either inert

diluents or as free-radical inhibitors which slow the oxidation processes and decrease the heat returned to the fabric surface. Those retardants which act in the condensed phase may operate by several mechanisms. They may inhibit the pyrolysis so that the cellulose does not break down to produce the small volatile molecules necessary for flame propagation. More commonly, however, they act to alter rather than inhibit this pyrolysis reaction. The alteration is such that the mode of pyrolysis is changed and lesser quantities of flammable gas are produced. Finally, they may also exert their effect in a physical rather than a chemical manner. In this case they act as a shield to prevent the transfer of heat from the flame back to the fabric surface. This reduces the rate of polymer pyrolysis and fuel production is decreased.

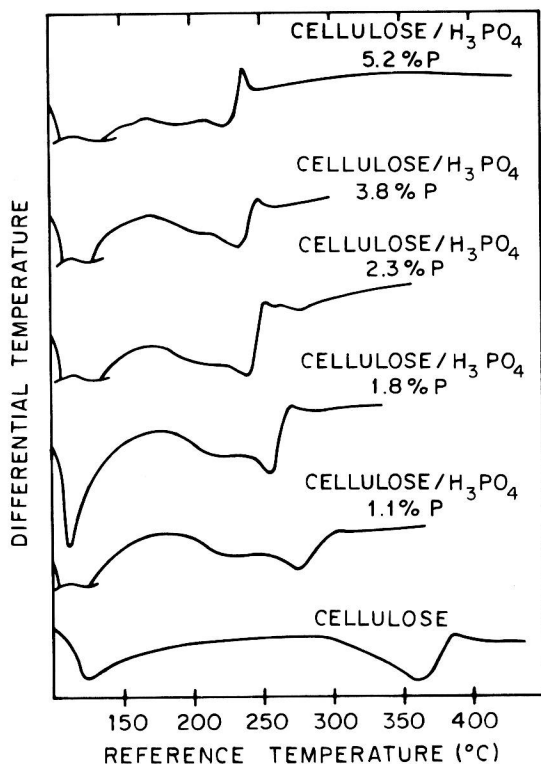
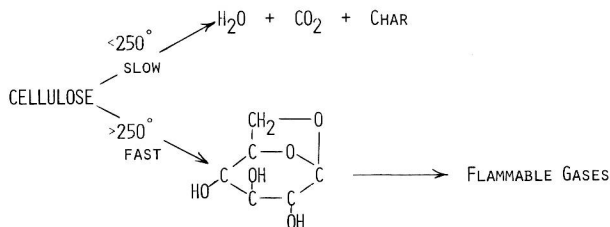


FIG. 1. Thermal analysis of cotton fabrics treated with various amounts of phosphoric acid [6].

In order to evaluate a particular flame-retardant system, it becomes necessary to determine the mechanism of action of the various flame retardants on the fabric. This usually requires a knowledge of whether the flame retardant is gas-phase or condensed-phase active. Once this is known, an investigation to determine the actual chemical mechanism involved in the retardation process may begin.

A wide variety of phosphorus-containing flame retardants are known to be effective on cellulosic substrates. Of these, phosphoric acid is one of the simplest and most effective. For many years, it has been postulated that this material acts completely in the condensed phase to alter the fuel-producing reaction. That this is actually the case has been shown in a recent study [5]. Thermal analysis of cotton fabrics treated with various amounts of phosphoric acid are shown in Figure 1. The DTA curves show that the endothermic pyrolysis reaction of the cellulose occurs at progressively lower temperatures as increasing amounts of phosphoric acid are present. In fact, the endothermic decomposition reaction becomes two endotherms in the presence of phosphoric acid. It has been suggested that these endotherms correspond to catalyzed decomposition and catalyzed phosphorylation of the cellulose [7]. This is possible in the case of cellulose because of its ability to undergo decomposition by at least two competing pathways, as shown in Scheme 1. The decomposition to carbon dioxide and water proceeds only very slowly in the absence of catalysts. In the presence of a catalyst such as phosphoric acid, however, this reaction becomes the predominant one at the expense of the fuel-producing reaction.

This reaction in fuel supply is reflected in the behaviour of these samples in the oxygen index tester. Fenimore and Martin have suggested that the oxygen index tester constitutes a good probe into flame-retardant mechanisms when more than one oxidation medium is used [8].



SCHEME 1. Decomposition of cellulose by two competing pathways.

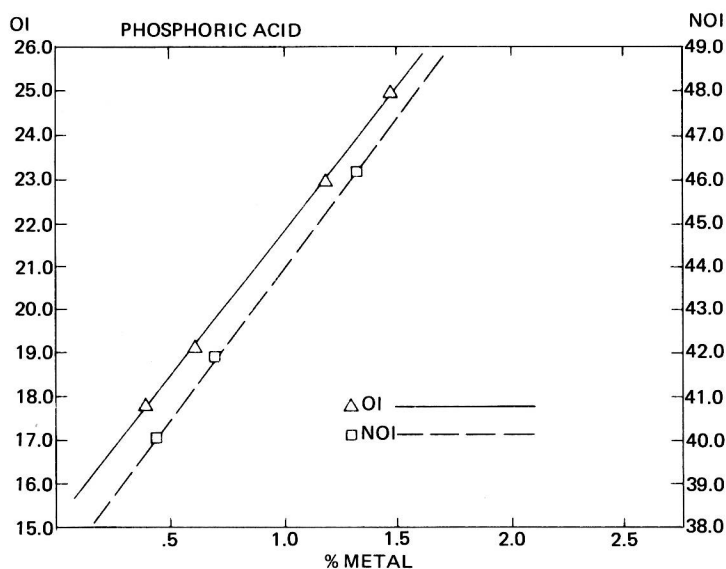


FIG. 2. Phosphoric acid-treated cotton [7].

If a flame retardant exhibits similar efficiencies in two or more oxidizing agents, it is generally considered that the flame retardant does not interact with the oxidant itself, but acts only to alter the amount of fuel supplied to the flame. That this is the case with phosphoric acid-treated cellulose can be easily seen from Figure 2. Measurements using oxygen and nitrous oxide as oxidants exhibit very similar dependency upon the concentration of retardants present, as shown by the parallel lines. These results together with the DTA results show quite conclusively that essentially all of the phosphoric acid activity is confined to the condensed phase. However, it is necessary to use both techniques in order to reach this conclusion.

This approach has been used quite successfully in several cases. For example, a number of transition metal salts are known to be good flame retardants for cellulosic fabrics, but their mechanism of action is almost completely unknown at present [9]. The oxygen index data in Figures 3 and 4 show that the molybdates and vanadates are particularly efficient even when compared with phosphoric acid [10]. This is surprising since most sodium salts of phosphorus acids are quite ineffective as flame retardants.



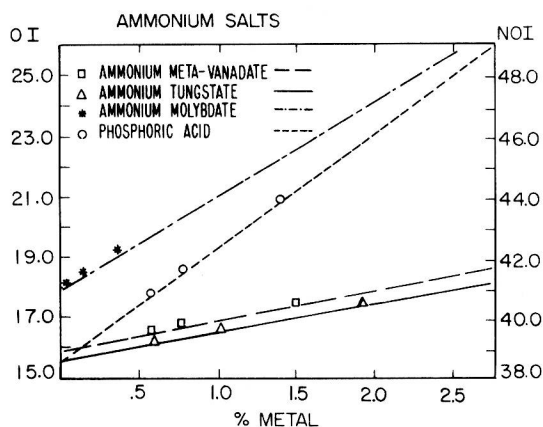


FIG. 3. Cotton fabrics treated with ammonium salts [9].

Differential thermal analyses (Figure 5) and thermogravimetric analyses (Figures 6 and 7) indicate considerable condensed-phase activity with both the sodium and ammonium salts [10]. Both series seem to be capable of catalyzing the cellulose decomposition and increasing the amount of residue remaining at the end of pyrolysis. This seems to be the most important activity of the retardants. Their effect

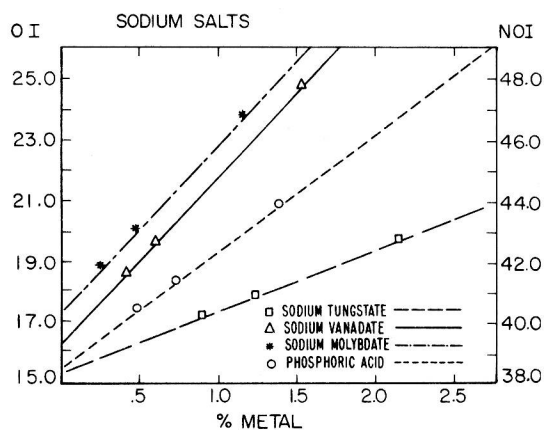


FIG. 4. Cotton fabrics treated with sodium salts [9].