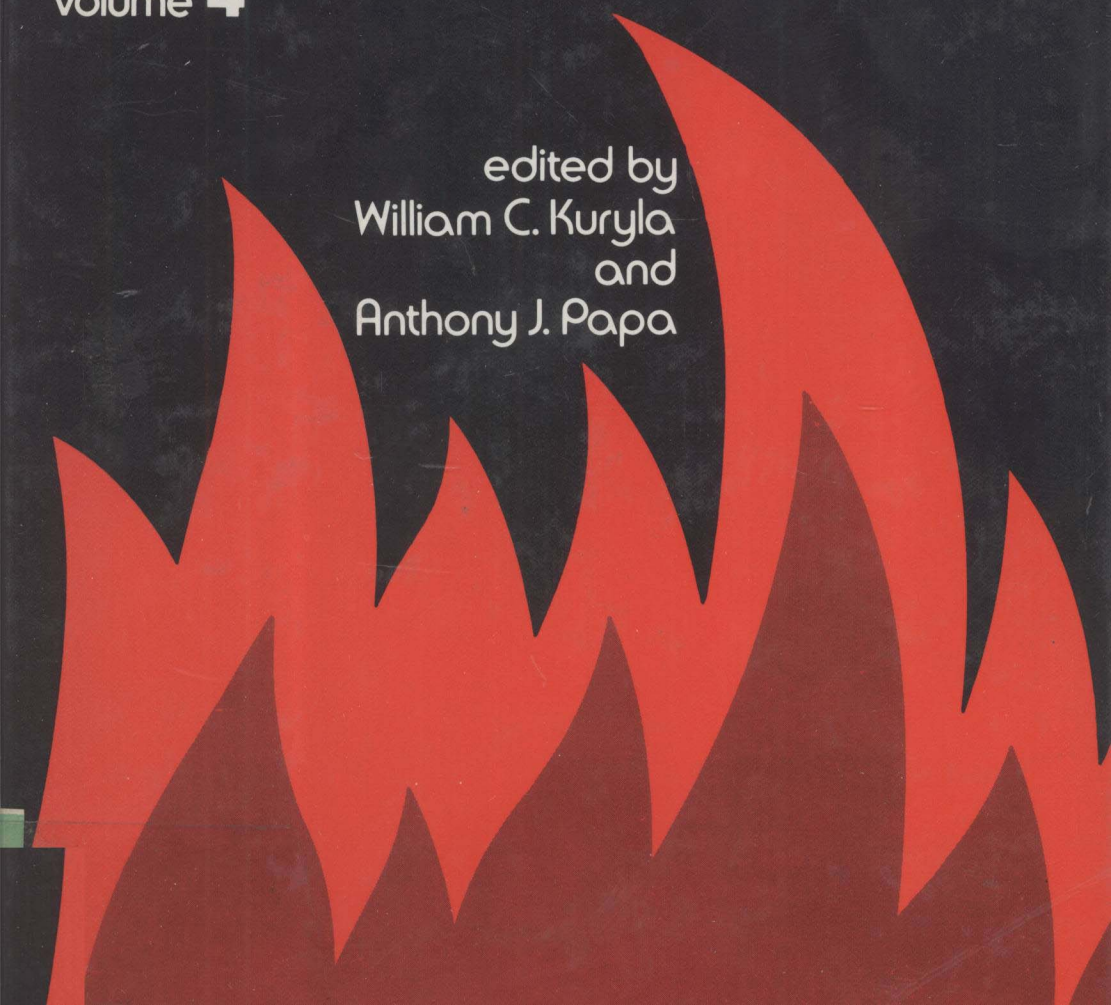


Flame Retardancy of Polymeric Materials

volume 4

edited by
William C. Kuryla
and
Anthony J. Papa




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P R E F A C E

The central theme of Volume 4 is focused on the mechanisms of flame retardancy.

The first chapter deals with general flame-retardant mechanisms, with a particular focus on intumescence and char formation. Flammability tests and terminology are reviewed together with a fundamental look at the burning process itself. General polymer flame-retardant mechanisms are examined, with emphasis on synergistic combinations of various materials and the effect of polymer structure on flammability. Intumescence and char formation is covered throughout the chapter and the use of intumescence coatings as an important method for protecting flammable substrates is discussed.

Chapter 2 provides a detailed view of the mechanisms of flame retardancy in a variety of polymers. A thorough review is given, and topics covered include mechanisms of polymer burning and the action of fire retardants. Fire retardants that alter smoldering and glowing combustions are a highlight in this chapter.

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CONTENTS OF OTHER VOLUMES

Contents of Volume 1

Available Flame Retardants, William C. Kuryla

Inorganic Flame Retardants and Their Mode of Action, James J. Pitts

Fire Retardation of Polyvinyl Chloride and Related Polymers, M. M. O'Mara, W. Ward, D. P. Knechtges, and R. J. Meyer

Fire Retardation of Wool, Nylon, and Other Natural and Synthetic Polyamides, Geoffrey H. Crawshaw, Alvin D. Delman, and Parvez N. Mehta

Contents of Volume 2

Fire Retardation of Polystyrene and Related Thermoplastics, Robert F. Lindemann

Fire Retardation of Polyethylene and Polypropylene, Robert J. Schwarz

Flame Retardation of Natural and Synthetic Rubbers, H. J. Fabris and J. G. Sommer

Flame Retardancy of Phenolic Resins and Urea- and Melamine-Formaldehyde Resins, N. B. Sunshine

x / Contents of Other Volumes

Contents of Volume 3

Flame-Retarding Polyurethanes, Anthony J. Papa

Flame-Retardant Acrylic Polymers, Sidney Melamed and Wayne E. Feely

Additivity, Synergism, and Antagonism in Flame Retardancy, Edward D.
Weil

Flammability and High-Temperature Characteristics of Composites,
Edward L. Wilson

Flame Retardancy of Polymeric Materials

Volume 4

CONTENTS

Preface	v
List of Contributors	vii
Contents of Other Volumes	ix
 1. THE IMPORTANCE OF INTUMESCENCE AND CHAR IN POLYMER FIRE RETARDANCE	 1
Raymond R. Hindersinn and Gilbert Witschard	
I. Introduction	2
II. Flammability Tests and Terminology	3
III. Fire Retardance and the Burning Process	10
IV. General Polymer Fire-Retardant Mechanisms	19
V. Intumescent Coatings and Their Effect on Fire Retardance	90
References	102
 2. MECHANISMS OF FIRE RETARDANCE IN POLYMERS	 109
David L. Chamberlain	
I. Introduction	110
II. The Burning of Polymeric Materials	111
III. Fire Retardance in Principle	112
IV. Fire Retardance in Practice	120
References	157

1

THE IMPORTANCE OF INTUMESCENCE AND CHAR IN POLYMER FIRE RETARDANCE

Raymond R. Hindersinn and Gilbert Witschard

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I. INTRODUCTION	2
II. FLAMMABILITY TESTS AND TERMINOLOGY	3
A. ASTM D 635-74 Test for Flammability of Self-Supporting Plastics	4
B. ASTM D 757-74 Flammability Test for Self-Extinguishing Plastics	5
C. ASTM D 1692-74 Test for the Rate and Extent of Burning of Cellular Plastics	5
D. ASTM D 2863-74 Oxygen Index Test	6
E. ASTM E 84-70 Test for Surface Burning Characteristics of Building Materials or Tunnel Test	8
III. FIRE RETARDANCE AND THE BURNING PROCESS	10
A. Fundamentals of the Burning Process	10
B. Fire-Retardant Methods	15
IV. GENERAL POLYMER FIRE-RETARDANT MECHANISMS	19
A. Halogen Fire Retardants	19
B. Hydrated Alumina	41
C. Effect of Polymer Structure on Flammability	42

D. Antimony-Halogen Synergism	50
E. Fire-Retardant Mechanisms of Phosphorus	67
F. Phosphorus and Halogens	79
V. INTUMESCENT COATINGS AND THEIR EFFECT ON FIRE RETARDANCE	90
A. Introduction	90
B. Intumescent Theory and Mechanism	91
C. Nonconventional Intumescent Coatings	97
D. Summary	102
REFERENCES	102

I. INTRODUCTION

The increasing public concern for the environment and the general safety has recently resulted in an enhanced concern for our mounting yearly fire losses of both life and property. The impact of the annual loss of about 12,000 lives and approximately \$2.5 billion in property [1] has led to increasing public pressure for governmental action to significantly reduce this drain on our resources. The recent broad amendments to the Flammability Fabrics Act of 1953 and the passing of Fire Research and Safety Acts are only two of the congressional responses to these needs of the public.

The need for improvements in the current fire safety and building codes is emphasized by the obvious inadequacy of modern building construction. The continued heavy losses of both life and property occurring in so-called "fireproof" buildings is epitomized by the heavy property loss (\$55 million) resulting from the fire in the General Motors Hydramatic Plant at Livonia, Michigan [2]. Here minor amounts of flammable furnishings and asphalt roofing led to the complete destruction of an all-steel, noncombustible building. The sagging of the steel reinforcing under the influence of the heat from the fire completed the destruction of the buildings and its contents.

A similar heavy property loss was recently reported from a fire in a new 50-story office building even before occupation was complete [3]. The complete collapse of two intermediate floors resulted from flammable furnishings and plastic insulation in the curtain wall construction. A major source of fuel for this fire was the molten plastic, feeding the fire and thus increasing its intensity. Again, major structural damage to the building resulted from the sagging of the structural steel under the influence of the heat.

Flammable textiles also contribute significantly to our yearly toll of death attributable to fire. More than 175,000 burn cases in 1969 were

caused from burning clothing with a yearly death toll of 4000 [4] resulting from such accidents. This again is a common hazard to life that could be significantly reduced by the application of technology already available.

Despite the known deficiencies of many conventional materials, the continued widespread replacement of these materials with the newer synthetic resins, fibers, and plastics has posed the realistic possibility of increasing an already serious fire hazard by the indiscriminate use of these relatively untried materials. A more thorough understanding of polymer and plastics flammability characteristics will be necessary if our fire safety record is to be improved in the future.

The economic incentive for improving our fire safety record is well documented. The attainment of such a goal would appear to be dependent upon a balance between the correct use of fire-retardant theory and technology, the setting of suitable flammability standards, and the appropriate modification and standardization of the many building codes currently in force. It therefore becomes imperative that we thoroughly understand polymer flammability and the related fire-retardant technology if we are to make the most intelligent and efficient use of polymers in the future. Although the primary objective of this critical review is to assess the importance of condensed-phase reactions in polymer flammability or lack thereof, it is hoped that the discussion will lead to a better understanding of the subject matter and contribute in some small way to the more intelligent application of these useful materials to reduce the future fire hazard without unduly limiting their potential for economically improving the esthetics, character, and quality of our future life patterns.

II. FLAMMABILITY TESTS AND TERMINOLOGY

A knowledge of some common flammability test methods is considered to be necessary for a complete understanding of the forthcoming discussion of fire-retardant mechanisms. A brief summary of the test methods referred to during this discussion is included for the convenience of the reader. Some of these tests have been developed to evaluate more conventional building materials and have subsequently been applied to polymers; other tests have been devised specifically for use on polymeric compositions.

Laboratory screening tests have been most generally used in fire-retardant research and will be most frequently referred to. These screening tests or small-scale tests compare burning rates of various plastics [5]. Such America Society for Testing and Materials (ASTM) tests as D 635-74, Flammability of Rigid Plastics, and D 1692-74, Flammability of Plastic Foams and Sheeting, fall into this category.

Occasional reference will be made to the ASTM E-84 tunnel test as the most common design or material test. It is not restricted to polymers. Since it attempts to classify materials under actual use conditions, it requires large samples and extensive test equipment.

Several of the tests discussed below have recently been significantly altered in character and report procedures. Generally, the main changes have been to remove such classifications as self-extinguishing and nonburning in order to conform to recent governmental rules [6]. The reader should be aware that the most recent test procedures are described and that the original work has been performed under the older specifications.

A. ASTM D 635-74 TEST FOR FLAMMABILITY OF SELF-SUPPORTING PLASTICS

This test is a standard method for obtaining comparative data on moderately fire-retardant polymeric materials. A sample capable of supporting itself in the horizontal position must be used in the test. The test apparatus is shown in Figure 1. A flame is touched to a specimen of the polymer for over 30 sec and then evaluated on the basis of the burning rate, average burning time, and extent of burning. A gage mark is placed on each specimen 100 mm from the ignition end of the specimen. The test is repeated until three specimens have burned to the gage mark or until 10 specimens have been tested. This test procedure has been modified recently to eliminate the burning, nonburning, and self-extinguishing classifications previously used to describe flammability behavior.

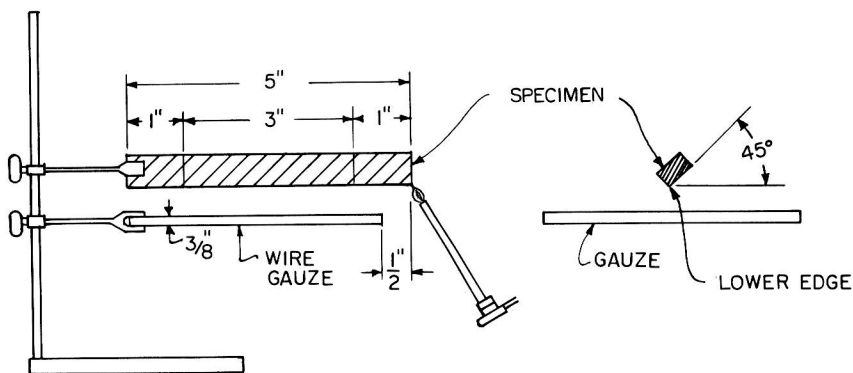


FIG. 1. ASTM D-635 test apparatus.

The most serious deficiencies of the test are that it fails to measure the actual fire hazard and that it fails to distinguish between polymers which do not drip and those which melt as the flame progresses down the sample, with quantities of the flaming, molten polymer falling away from the test sample in the process. This distinction is very important since the flame can be spread by this drip. Moreover, flammable polymers can obtain low burning rates and extents of burning by this test if the flame front is carried away by the falling drip.

B. ASTM D 757-74 FLAMMABILITY TEST FOR SELF-EXTINGUISHING PLASTICS

This test was developed specifically for the comparisons of rigid plastic sheets or plates greater than 1.3 mm thick. This test follows ASTM D 635 in increasing intensity and was found to be necessary because of the wide differences in flammability of plastics evaluated by the latter test. The test specimen is brought into contact with an igniting bar heated electrically at 950° C for a period of 3 min or until the specimen ceases to burn. At the end of this test period, any flame remaining is extinguished and the burning rate in millimeters per minute is calculated from the length of the burned part of the specimen for those specimens which continue to burn for the 3-min test time. The burning time in seconds and the extent of burning in millimeters are reported for the others.

This test is chiefly useful for the more fire-retardant nonmelting compositions. Good fire retardancy by this test is indicated by burning rates of less than 0.3 in. /min, while burning rates of less than 0.2 in. /min indicate the more highly fire-retardant compositions.

C. ASTM D 1692-74 TEST FOR THE RATE AND EXTENT OF BURNING OF CELLULAR PLASTICS

Materials which shrink or cure under the heat of the test conditions cannot be evaluated by this test. A flame is applied to the test specimen for a period of 60 sec, and according to the results, the burning rate (mm/sec) or the burning time (sec) and the extent of burning in millimeters is reported for the polymer. The apparent cause which extinguished the flame, such as dripping, melting, etc., is also noted.

This test, although useful for the purpose intended, is carried out under relatively mild conditions that can result in low burning rates for foams with a relatively wide variation in fire retardancy. For example, 20-30% of ordinary, expanded polystyrene samples will pass the test with a low rating because the rapid shrinkage of the foam away from the flame results in a

failure to ignite adequately for continued burning. The metal used as a specimen support also undoubtedly contributes considerably to the extinguishment of the sample by removing a significant amount of the heat of combustion.

D. ASTM D 2863-74 OXYGEN INDEX TEST

The oxygen index test method determines the relative flammability of plastics by measuring the minimum oxygen concentration in a slowly rising mixture of oxygen and nitrogen that will just support combustion of a candle-like sample of the material to be evaluated. Its significant advantage over previously used laboratory test methods is that it yields a reproducible and accurate numerical rating that can be determined for a considerable variety of polymer compositions with a wide range of burning characteristics. A schematic drawing of the test apparatus is indicated in Figure 2.

The minimum oxygen concentration or oxygen index is measured under equilibrium conditions which are established by the balance between heat

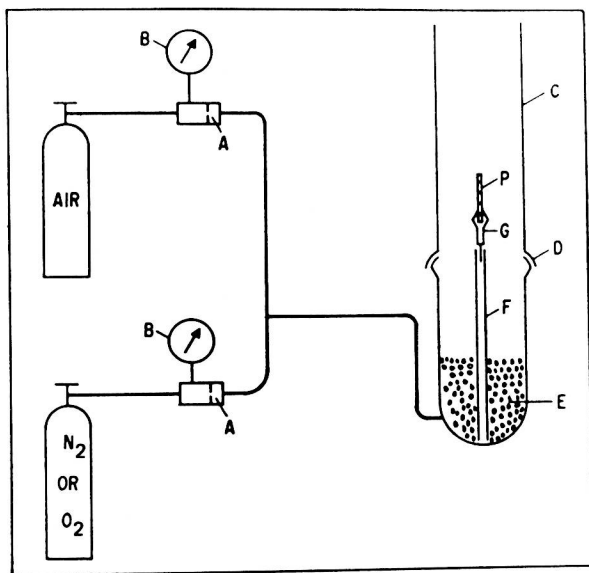


FIG. 2. Schematic diagram of the oxygen index apparatus (A, metering orifice; B, Bourdon test gate, 0-100 psig; C, pyrex tube, 3.5 in. i.d.; D, tapered ground glass joint; E, bed of glass beads; F, pyrex tube, 7-mm i.d.; G, spring clamp; P, polymer sample, about $0.6 \times 0.3 \times 8$ cm).

TABLE 1. Oxygen Indexes (n) of Various Materials

Material	n
Polyoxymethylene	
Delrin, Du Pont	0.150 ± 0.003
Celcon, Celanese	
0.1 cm thick	0.148 ± 0.001
Polyethylene oxide,	
Polyox WSR-35, Union Carbide	0.150
Kitchen candle (wick in paraffin)	0.16
Polymethyl methacrylate,	
Plexiglas, Rohm and Haas	0.173 ± 0.001
Polypropylene,	
Profax 6506, Hercules	0.174 ± 0.002
Asbestos-filled, "slow burning"	
JMDC-4400, Union Carbide	0.205 ± 0.005
"Self-extinguishing" JMDA-9490,	
Union Carbide (probably contains chlorine and antimony oxide)	0.282 ± 0.003
Polyethylene,	
1220, Allied Chemical	0.174 ± 0.001
Polystyrene,	
0.1 cm thick from stock	0.181
Polybutadiene, cross-linked with two parts of dicumyl peroxide	0.183
Polyvinyl alcohol, Elvanol 70-05, Du Pont	0.225 ± 0.004
Chlorinated polyether, Penton, Hercules	
-CH ₂ -C(CH ₂ Cl) ₂ -CH ₂ -O-	0.232
Polycarbonates, various clear Lexan resins.	
General Electric -C ₆ H ₄ -C(CH ₃) ₂ -C ₆ H ₄ -OC(O)-	0.26 to 0.28
Polyphenylene oxide, General Electric	
-C ₆ H ₂ (CH ₃) ₂ -O-	0.28 to 0.29
Carbon	
Porous carbon, PC-25, National Carbon	0.559 ± 0.003
Carbon electrode, L 8109, National Carbon	0.635
Silicone rubber, General Electric	0.30 to 0.33
Polyvinyl chloride, Geon-101 without plasticizer,	
Goodrich	0.45
Polyvinylidene chloride, Saran 281S905, Dow	0.60
Teflon, Du Pont	0.95

produced from the combustion of the specimen and the heat lost to the surroundings. The equilibrium point is approached from both sides of the critical oxygen concentration in order to establish the oxygen index. The test procedure consists of igniting the top of the specimen in the test apparatus under some oxygen concentration, which is chosen by past experience or in an arbitrary manner. The oxygen concentration is then reduced if the specimen burns for 3 min or more, or more than 50 mm. Conversely, the oxygen concentration is increased if the specimen extinguishes before burning 3 min or 50 mm. This procedure is then repeated until the lowest oxygen concentration is determined in which extinguishment occurs at 3 min or after 50 mm of burning. The oxygen index is calculated from data obtained from a series of triplicate determinations.

Table 1 shows representative results obtained by Fenimore and Martin [7] by this method for a variety of polymers. The versatility of the method is indicated by the fact that highly flammable polyoxymethylene and non-flammable polytetrafluoroethylene (Teflon) are readily evaluated.

E. ASTM E 84-70 TEST FOR SURFACE BURNING CHARACTERISTICS OF BUILDING MATERIALS OR TUNNEL TEST

This test, developed by Underwriters' Laboratories, Inc., is used to determine the surface-burning characteristics of any building material that is capable of supporting itself in position on the roof section of the test furnace. The test correlates the burning characteristics of the material directly to its behavior under some use conditions and is especially important since many governmental codes require an Underwriters' label for general use of a material in public buildings. The test apparatus consists of a chamber 25 ft in length and 17.5 in. \times 12 in. in cross section, one end of which contains two gas burners (Figure 3). A 25-ft \times 17-in. test sample is exposed to the gas flame for 10 min, while the maximum extent of the flame spread and the temperature down the tunnel are observed. The flammability is then calculated on an arbitrary scale of 0 to 100 with red oak being assigned a value of 100 on this scale and asbestos, a zero.

In addition to flame spread, the test has been modified to yield a measure of smoke evolution and heat contribution of the material by the installation of a photoelectric cell and thermocouple in the exhaust stack downstream from the test specimen. The smoke density and temperature of the exhaust gases are measured continuously and assigned a value relative to the behavior expected in a standard evaluation of red oak.

This test has come under considerable criticism recently because of its designation of such highly flammable plastics as foamed polystyrene (fire-retardant grade) as class 1 or incombustible by this test. Although the