Chemical Modification of Polymers with Flame-Retardant Compounds

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I. INTRODUCTION

The science and technology of synthetic polymers has undergone explosive growth in the last few decades, and the number of different polymeric materials in our built environment increases almost daily. All organic polymers burn, and thus entail some measure of fire hazard in some situations. With increasing awareness of the nation's fire problem (Report of the President's Commission on Fire Prevention and Control, *America Burning*, 1973), it has become evident that the problems associated with flammability of polymeric materials must be attacked—and solved. With the large number of polymers in commercial use, problems of flammability and fire retardation are complex and multifaceted.

Tables I and II indicate types and volumes of fibers and plastics produced in the U.S. To substitute polymers with improved fire performance, where required, either thermally stable new polymers of satisfactory performance

TABLE I
U.S. Man-made Fiber Production in 1973

Fiber	Billion Pounds
Rayon	0.89
Acetate	0.46
Nylon	2.18
Polyester[a]	2.77
Olefin	0.42
Acrylic	0.74
Glass	0.69
Other	0.13
Cotton[b]	3.65
Wool	0.17

[a]Source: Textile Organon, Jan.-Feb. 1974, Textile Economics Bureau, Inc., New York.
[b]Source: U.S.D.A. Economic and Statistical Analysis Division in Textile Highlights, December 1973, American Textile Manufacturers Institute, Inc., Washington, D.C.

properties have to be developed, or existing polymers must be modified by addition of fire-retardant compounds. The latter, short-range approach, is more important, technologically and commercially, at this time.

Modification of known polymers may involve either a coating applied to the surface of the material, or the incorporation of a fire-retardant component into its bulk at an appropriate stage of manufacture.

During the last few years, many new concepts relating to flammability and fire retardants in polymers have evolved from research investigations in government, university, and industrial groups. Much progress has been made in the development of principles, hypotheses, materials, and methodology. These technical accomplishments, stimulated in part by the pressure of legislative action, and by new standards for flammability performance in use, in many instances have included short-range, pragmatic solutions to problems which were not adequately understood or defined. Much work remains to be done, much is being done, and the state of the art in this field of chemical technology is a rapidly changing one.

II. DEFINITION OF TERMS

Lack of precision in the use of terms related to polymer flammability, polymer combustion, etc., has been noted by several authors (Miller, 1973;

TABLE II

Plastics Sales in the U.S. for 1973 and 1974*

Material	1973	1974
Acrylic	233	243
Alkyd[a]	334	388
Cellulosics	77	76
Coumarone-indene and petroleum resins	160	160
Epoxy	102	106
Nylon	87	88
Phenolic	624	587
Polyester	468	425
Polyethylene, high density	1,248	1,275
Polyethylene, low density	2,691	2,769
Polypropylene	1,012	1,061
Polystyrene and styrene copolymers	2,356	2,328
Polyurethane	593	622
Polyvinyl chloride and copolymers	2,151	2,180
Other vinyls	390	420
Urea and melamine	488	475
Others[b]	138	147
Total	13,152	13,350

*In metric tons $\times 10^3$. Source: *Modern Plastics*, Jan., 1975.

[a]Includes captive consumption, about 50%.

[b]Includes polyacetal, polybutylene, fluoroplastics, polycarbonate, silicones, thermoplastic polyesters, thermoplastic urethanes, and others.

Nelson et al., 1974). Some efforts are currently underway to define and standardize the use of terms and to produce a glossary with definitions in several languages. Until these definitions are decided on, and utilizing such working documents as have been produced by task forces and committees in the course of these efforts,*† terms used in this review are defined in this section in the hope that ambiguity and misunderstanding will be avoided.

A. Thermal Degradation and Combustion

Thermal degradation. Irreversible chemical decomposition due to increase in temperature.

* See *Textile World*, June 1975, pp. 107, 109.

† Glossary in preparation by the Ad Hoc Committee on fire safety aspects of polymeric materials, National Materials Advisory Board, National Academy of Sciences.

Pyrolysis. Irreversible chemical decomposition due to increase in temperature without oxidation.

Combustion. Self-catalyzed exothermic reaction involving two reactants (fuel and oxidizer).

Fire. Uncontrolled combustion.

Flames. Gas-phase combustion processes with emission of visible light.

Ignition. Initiation of combustion.

To Glow. To burn without flame, but with visible light.

B. Chemical Modification

Comonomer. Compound added *in* polymer synthesis and becoming a part of the polymer molecule.

Additive. Compound added *after* the polymer has been synthesized but before or during its conversion to final form (e.g., fiber, plastic); not covalently bound to polymer substrate.

Finish. Compound or combination of compounds added *after* conversion to end product (e.g., fiber, fabric). May be covalently bound or deposited.

Effectiveness. Ability of flame retardant to decrease flammability of the polymer substrate in which it is present.

Synergism. Observed effectiveness of combinations of compounds *greater* than the sum of the effects of individual components.

Antagonism. Observed effectiveness of combinations of compounds *smaller* than the sum of the effects of individual components.

C. Polymer Flammability

Afterglow. Glowing combustion in a material after cessation (natural or induced) of flaming.

Autoignition. Spontaneous ignition of a material in air.

To Char. To form more or less pure carbon during pyrolysis or incomplete combustion.

Ease of Extinguishment. Relative facility with which a given material, once burning, can be extinguished.

Ease of Ignition. Measure of the time or temperature at which sustained flaming of a material in air occurs (with reference to material dimensions and density, incident heat flux and air composition, temperature and velocity).

Fire Resistance. Capacity of a material or structure to withstand fire without losing its functional properties.

Flame Resistance. Property in a material of exhibiting reduced flammability.

Flame Propagation. Spread of flame from region to region in a combustible material (burning velocity = rate of flame propagation).

Flame Retardant. Chemical compound capable of imparting flame resistance to (reducing flammability of) a material to which it is added.

Flammability. Tendency of a material to burn with a flame.

Glowing combustion. Oxidation of solid material with light, but without visible flame.

Self-extinguishing. Incapable of sustained combustion in air after removal of external heat or flame (with reference to material dimensions, orientation and ignition).

Smoldering. Combustion without flame, but usually with incandescence and smoke.

Smoke. Fine dispersion in air of particles of carbon and other solids and liquids resulting from incomplete combustion.

Toxicity. Harmful effect on a biological system caused by a chemical or physical agent.

D. Test Procedures

(Limiting) oxygen index. Minimum percent oxygen in the environment which sustains burning under specified test conditions.

Vertical, horizontal, 45° [test]. Orientation of the test specimen during flammability test under specified conditions.

Self-extinguishing. Does not continue to burn under the specified test conditions after the source of ignition is removed (under specified test conditions).

Flame spread. Extent of propagation of flame in space or over specimen surface under specified test conditions.

Char length. Length of totally or partly burned material after exposure of a specimen to a flame (under specified test conditions).

Rate of heat release. Amount of heat released per unit time by specimen burning under specified test conditions.

III. SCOPE OF THE REVIEW

A. Subject Matter

The technical literature covering various aspects of polymer flammability, of flame-retardant compounds for polymers, and of possible improvements in the fire safety of our environment has undergone explosive growth in the last decade. Many review articles, books, and conference proceedings have recorded and reviewed scientific and/or technological developments in various ways. One might therefore question the usefulness of yet another review of this important and growing field. However, the subject matter is so vast, inherently interdisciplinary, and complex, that each review inevitably presents a limited treatment, motivated by the specialized knowledge and approach of the author, and therefore primarily of value to those having similar interests and research goals. The present article is no exception. It addresses primarily concepts in the chemical technology of flame retardation of polymers—and it attempts to review problems, approaches, and state of the art for this seg-

ment of the problem. Even with this limitation, a systematic and comprehensive coverage of the subject matter is difficult. On one hand, the molecular structure of the polymers and of the flame retardants are essential considerations in discussing the thermal degradation and combustion of specific polymer/flame-retardant systems. On the other hand, the application or end-use of a specific polymer (e.g., fiber vs. plastic) is an overriding consideration in the definition of all the properties required, including those which are affected by the presence of flame retardants. In an attempt to acknowledge and discuss these two levels of systematic classification of the subject matter, this review covers polymers in six broad technological (or application) categories (wood, fibers and fabrics, plastics, cellular plastics and foams, elastomers, and coatings) and, within each category, the chemical types of major importance. This will allow discussion of specific problems of flammability and flame retardation of the polymer in terms of its molecular structure *and* its application. Polymers covered in this review are those which exhibit moderate or low thermal stability, and undergo thermal degradation when exposed to temperatures of below about 300° C for brief periods, even in the absence of an oxidative environment. Although the mechanism of pyrolysis and thermal degradation of polymers differs for specific macromolecules, most known natural and synthetic polymers are not thermally stable in this temperature range (Madorsky, 1964): the subject matter discussed here thus includes an overwhelming proportion of the commercial polymers of the 1970s.

This review does *not* include discussion of high-temperature resistant organic polymers in which thermal stability of the macromolecule is an intrinsic structural feature, generally attained by incorporating thermally unreactive ring structures in the polymer chain.

These polymers can preserve their structural integrity and retain useful properties over long periods of time at temperatures of about 300° C, or for brief periods at temperatures approaching 1000° C (Nelson et al., 1974). The principles used in the synthesis of thermally stable polymers have been surveyed in several recent reviews and monographs (Frazer, 1968; Jones et al., 1970; Black, 1970; Van Krevelen, 1975), to which the interested reader is referred. While these materials currently represent a category of "high-performance" or "specialty" polymers which are available in limited quantities, and are costly, their availability and commercial importance could increase at a rapid rate with increasing awareness of the improved fire safety they may offer in specific end-uses.

In defining the scope of this review, it is important to point out that *no* attempt has been made to list and discuss the numerous test methods which have been proposed for the evaluation of polymer flammability in the laboratory, and in simulations of fire accidents on various scales. The methodology of testing for polymer flammability, the significance of test results, and their correlation with fire hazard form a complex subject which is beyond the scope of this review, and best discussed by physicists and engineers. However, polymer flammability is not an intrinsic property of the material and the behavior of a given polymer or material in relation to fire stress can be de-

scribed in quantitative terms only with reference to specific test methods or evaluation procedures. Some conceptual problems associated with flammability testing of polymers have been reviewed (Steingiser, 1972; Meisters, 1975). Generally speaking, however, test methods for flammability are designed with reference to a particular application of the material, and test methods proposed for specific applications (e.g., textiles) have been reviewed in this vein (Benisek, 1975). Notwithstanding the usefulness of these reviews, they do not generally provide an adequate background for discussion of polymer flammability in definitive terms, and descriptive, or qualifying terminology must be used. In the review which follows an effort will be made to specify the test method used (and to provide appropriate reference to it) whenever the effects of flame retardants on polymer flammability are discussed. Whenever possible, an indication of the significance of the test results reported will be included. However, since the discussion will be generally limited to polymers and polymer/flame-retardant combinations evaluated by laboratory methods, such indications will not necessarily be of value in assessing the probable or expected behavior of the polymers when used in practice, especially in conjunction with other materials. Knowledge of the flammability behavior of a polymer in the laboratory is only the first step in the knowledge required for the assessment of the flammability behavior of the polymer in use and, eventually, of the relative fire hazard posed by different polymers in realistic applications.

B. Classification of Subject Matter

For the convenience of the reader in proceeding from the general to the specific, the subject matter of this review has been classified (somewhat arbitrarily) as follows.

Sections IV–VII present a general background discussion and information on the subjects of polymer degradation (IV), flame-retardant compounds (V), approaches and problems in chemical modification of polymers (VI), and polymer applications where flame retardants and fire safety are considered to be of interest (VII).

Sections VIII–XIII discuss flame-retardant modification for specific polymer applications, namely, wood (VIII), fibers (IX), plastics (X), foams (XI), elastomers (XII), and coatings (XIII). The extent and depth of these discussions vary greatly, reflecting *both* the relative importance of fire safety for the polymer application discussed, *and* the state of the art on modification of the specific product type with flame retardants.

The emphasis placed on each polymer class within each section is, on the other hand, primarily a reflection of the current state of the art.

C. Selection of References

The *selection* of references of major scope and significance from the many

thousands which exist on the subject has been a major objective of this review. Critical selection can be a service to the reader, but inevitably entails the author's judgment with regard to the relative importance of investigations and technical publications. In making this judgment, the author has been guided by the following assumptions and rationale: (1) Existing critical reviews and books have been cited freely, indicating specific pages, sections, or compilations in the context of the discussion. (2) Literature references covering original investigations on some aspects of the subject have been cited when these were considered to be significant contributions to knowledge or technological development in the field. References to narrow, specific, or procedural studies have *not* been included. (3) In the text, references to patent disclosures have been included only in those instances where a corresponding literature reference was not available, *and* the material was considered important. In other words, mere listing of patent disclosures has been generally avoided in the text. References to patent disclosures are included in tabulations and summaries which show examples of flame-retardant compounds, reactions, or processes. Cited patents in this case are intended as illustrative, and will serve the reader as a starting point for searching relevant patent literature further. (4) Whenever possible, the *first* technical publication covering a specific concept or compound or process has been selected for citation. In most instances, this first disclosure of a new concept is followed by many elaborations, improvements, and variations which have not been included in the bibliography, but can be found in most instances in the cited reviews.

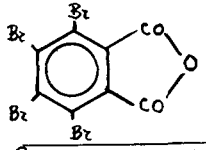
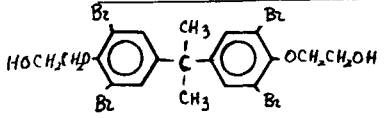
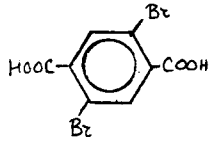
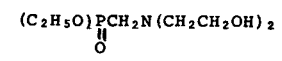
IV. PYROLYSIS, THERMAL DEGRADATION, AND COMBUSTION

The study of polymer combustion and of the means of retarding it (flame retardation) requires knowledge of thermal degradation, including pyrolysis (thermal degradation in an inert atmosphere), and thermal-oxidative degradation processes. These processes depend on polymer properties which are primarily determined by molecular structure, and thus specific for each polymer type. Decomposition temperature, rate of thermal degradation under specified conditions of heating and environment, composition of pyrolysis products and of the products of combustion depend on the chemical structure and composition, and are affected by the flame-retardant species present, and by other modifiers, if any. On the other hand, thermal degradation, ignition, and combustion processes for organic polymers can be represented schematically by the general sequences shown in Fig. 1 (p. 311) (Einhorn, 1971) with thermally induced decomposition clearly preceding ignition.

Fundamental knowledge of the thermal degradation of organic polymers has been compiled in a classic book by Madorsky (1964), and more recently discussed in monographs (Conley, 1970), symposia proceedings (Wall, 1973), and in an excellent review (Fristrom, 1974). The latter article includes a clear

TABLE III

Examples of Flame-Retardant Compounds Used as Comonomers

Compound(s)	Polymer	Used in Application	Reference
$CH_2 = CH\ Cl$, $CH_2 = CH\ Br$	Polyacrylonitrile	Fibers	USP 3,487,058 (1969) Mark et al., 1968, Vol. 3, p. 199.
	Polyester (unsaturated)	Resins	Stepniczka, 1976.
	Polyethylene terephthalate	Fibers	USP (to Emery Ind.) 3,794,617 (1974).
	Polyethylene terephthalate	Fibers	I.P. Nelson, 165th National Meeting, ACS, Dallas, Texas (1973).
	Polyurethane	Rigid Foams	USP (to Stauffer Chem) 3,294,710 (1966), 3,235,517 (1966), 3,076,010 (1963).

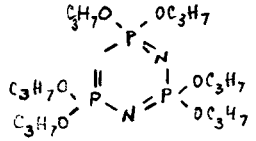
view of types of thermal decomposition, reaction regions in polymer combustion, solid-phase and gas-phase reactions as part of a generalized discussion of fundamental concepts which are essential for adequate understanding of flammability and flame retardation in polymers.

The mechanism and the course of thermal degradation have been studied extensively for specific polymers, particularly for cellulose. In the case of cellulose, considerable insight has been gained (Shafizadeh, 1968), and the effectiveness of specific flame retardants can now be explained in the context of a reasonable understanding of the mechanism of thermal degradation processes (Hendrix et al., 1970; Walker, 1970). The thermal degradation of polyacrylonitrile and of copolymers of acrylonitrile has been the subject of extensive investigations (Grassie et al., 1970–1973).

A catalogue of the numerous studies of thermal degradation of specific polymers and polymer compositions is beyond the scope of this review. It is appropriate to point out, however, that the thermoanalytical tools used to investigate thermal degradation in polymers have been greatly refined in

TABLE IV

Examples of Flame-Retardant Compounds Used as Additives

Compound(s)	Polymer	Used in Application	Reference
Sb_4O_6	synergist for halogenated compounds see Kuryla - Papa, 1973, Vol. 1, pp. 133-194	Cotton test fabrics, coatings, polyurethane foams	Little, 1947 J. Kestler, Modern Plastics 44(1), 102(1966), 47(9), 96(1970).
$[-(CH_2)_x - (CH)_y-]$ (Cl) chlorinated paraffin	Cellulose unsaturated polyester	Wood alkyd resin coatings	Canadian Patent 803,409 (1969), Touval (1972).
$(BrCH_2CHBr\ CH_2O)_3P=O$ Tris-2,3-dibromopropyl phosphate	Cellulose acetate and triacetate	Fibers	USP3,471,318(1969), USP3,321,330(1967), USP3,266,918(1966).
	Regenerated cellulose (rayon)	Fibers	USP3,455,713(1969).

recent years. Coupled with new, sensitive instrumentation for the analysis of degradation products, and of transient species in flames, these tools have been invaluable in providing needed understanding of thermal degradation processes and of the manner in which these are affected by flame retardants.

V. FLAME RETARDATION AND FLAME RETARDANTS IN POLYMERS

A. Principles

Recent books on fire retardants (Kuryla and Papa, 1973, 1975; Lewin et al., 1975; Lyons, 1970a) include references and discussion on most compounds suggested as fire retardants for polymeric materials. These books also summarize present knowledge and speculation regarding the mode of action of flame-retardant compounds, and current views, often controversial, regarding mechanisms of flame retardation in specific polymer systems. Generally speaking, the flammability of polymers can be decreased either by al-

tering the products of thermal decomposition in such a way that the amount of nonflammable combustion products is increased at the expense of flammable volatiles (solid-phase retardation), or by inhibiting oxidation reactions in the gas phase through trapping of free-radical species (gas-phase retardation), or by a combination of these mechanisms. Most experimental observations reported in the literature can be explained with reference to these two mechanisms. Nevertheless, other modes of effectiveness of flame retardants play a role, at least in specific systems (Kuryla and Papa, 1973): (1) generation of noncombustible gases, which dilute the oxygen supply at the surface of the burning polymer; (2) endothermic reactions of degradation products from the flame retardants with species present in the flame or substrate; (3) endothermic decomposition of the flame retardant; (4) formation of nonvolatile char or glassy film barrier, which minimizes diffusion of oxygen to the polymer substrate and also reduces heat transfer from flame to polymer substrate.

The mechanisms of flame retardation outlined above do not contradict each other, since several principles can simultaneously contribute to the effectiveness or action of a particular flame-retardant system. Furthermore, combinations of flame-retardant species may be deliberately designed to include several modes of action in a given polymer substrate: typically, combinations of phosphorus and halogen are widely used, and it is postulated that flame-retardant effectiveness of systems containing these elements includes a solid-phase effectiveness component (phosphorus) as well as vapor-phase activity (halogen).

In considering combinations of flame retardants, it is also important to point out the widely discussed but poorly understood phenomena of synergism. An excellent review of the subject is given by Weil in Kuryla and Papa (1975). As correctly pointed out by this author, the definition of synergistic effect (namely, an observed effect of a combination of flame retardants which is greater than the sum of the effects of the components) is deceptively simple, and the term "synergist" has been frequently misused in the literature on flame retardants. Definitive proof of true synergistic interactions of flame retardants is not available, but a critical study of the literature suggests that the synergistic effects of halogen and antimony in polyesters (Pitts et al., 1970), of phosphorus and nitrogen in cellulose (Tesoro et al., 1968, 1969) are significant, while synergistic interactions of phosphorus and halogen are questionable, and apparent synergism of halogen compounds with peroxides and other free-radical-generating compounds in hydrocarbon polymers is almost certainly an artifact caused by reduced viscosity and dripping of the melt.

B. Flame-Retardant Compounds

Flame-retardant compounds, in order to be useful, must fulfill complex sets of requirements, many of which are specific for each product. In most instances, these requirements can be met only in part, and some tradeoffs

become necessary. In principle, in order to be seriously considered, a flame retardant added to a polymer should (1) reduce flammability as compared to the unmodified polymer to a level specified for the product in terms of product performance in a specific flammability test; (2) reduce (or, at least, not increase) smoke generation, under specified conditions of testing: (3) not increase the toxicity of combustion products from the modified polymer as compared to the unmodified polymer; (4) be retained in the product through normal use (including exposure, cleaning, aging, etc.); and (5) have acceptable or minimal effect on other performance properties of the product in use (as established by relevant specifications).

In addition, consideration must be given to the effects which the added flame retardant may have on processing conditions, fabrication and costs in the manufacture of the modified product, to health hazards which may result from the presence of the compound in the work place, in the product, or in the environment (industrial hygiene, physiological effects, and ecological considerations, respectively), and, of course, to availability and economics of the flame retardant itself.

This formidable list of requirements readily explains why the number of commercially significant flame-retardant compounds is extremely small compared to the number of compounds which have been proposed and tested in the laboratory, reported in the technical literature, and shelved due to failure in one or more critical properties. Flame-retardant compounds of value have been identified or discovered primarily by trial and error, rather than on the basis of fundamental investigations of mechanism, or of systematic studies relating the parameters of molecular structure to flame-retardant effectiveness. The technology of flame-retardant compounds and flame-resistant polymeric materials is well advanced, while scientific principles of flame retardant classification are lacking. Known flame-retardant compounds may be grouped as follows:

(I) Inorganic acids and acid-forming salts (e.g., ammonium salts of sulfuric, sulfanic, phosphoric, hydrochloric, hydrobromic, and boric acid), which act as dehydrating agents. These are solid-phase retardants, of importance where durability to leaching or washing is not required (e.g., wood, textile cellulose, and paper).

(II) Inorganic salts which contribute to the formation of glassy coatings around the decomposing polymer mass (e.g., borates, phosphates, and silicates).

(III) Inorganic salts and hydrates which decompose endothermically, releasing a noncombustible diluent (e.g., water) into the gas phase [e.g., hydrated alumina ($Al_2O_3 \cdot 3H_2O$)], of importance in specific applications of thermoplastic resins (e.g., carpet backings).

(IV) Antimony compounds, which interact synergistically with halogen-containing flame retardants. The most important, antimony trioxide (Sb_4O_6) is extensively used in plastics and in fibers to reduce the amount of halogen-containing retardant needed, and thus minimize the effects of the modification on performance properties.

(V) Organic compounds of phosphorus—generally solid-phase retardants—which are important for cellulose polymers and polyurethane polymers. The organic moiety in these flame-retardant compounds contributes compatibility and/or reactivity with the substrate, while flame-retardant effectiveness and efficiency generally depend on the phosphorus content.

(VI) Organic compounds of halogen—generally gas-phase retardants—important for hydrocarbon polymers and others. Effectiveness and efficiency depend on the specific halogen (Cl vs. Br), on the halogen content, on the temperature at which dehydrohalogenation of the compound occurs (thermal stability of the halogen compound, aliphatic vs. aromatic halogen) in relation to the temperature of decomposition of the polymer substrate, and on the presence of synergists (e.g., antimony).

(VII) Organic compounds containing both phosphorus and halogen.

(VIII) Miscellaneous compounds which reportedly have shown effectiveness in specific substrate polymers under some conditions of measurement [e.g., tin, titanium, and chromium compounds (wool); molybdenum salts; zinc and magnesium chlorides (wood); and thiourea and ammonium thiocyanate (nylon)].

C. Chemical Modification with Flame Retardants

In the processing sequence of monomers to polymers, and, subsequently, to fibers, plastics, or other end products, flame retardants can be introduced in several ways. Each approach has advantages and limitations, which depend on many factors including processing requirements, properties of the flame retardants, level of flame resistance needed, critical product properties, etc.

The approaches that may be considered are briefly outlined below.

(1) Use of flame-retardant *comonomers* in polymer synthesis. The obvious advantage of this approach is that the flame retardant becomes an integral part of the polymer molecule, is resistant to leaching or removal, and thus to loss of effectiveness in use. The disadvantage resides in the effect of resulting changes in the polymer structure on polymer properties including morphology (orientation, crystallinity, intermolecular forces) and mechanical behavior (tensile strength, recovery), as well as physical properties such as melting point and glass-transition temperatures. The consequences of such effects are particularly important in fibers. Comonomers have been used commercially as flame retardants in acrylic fibers, in polyester fibers, and in polyurethane foams.

(2) Use of flame-retardant *additives* in the polymer, such additives being introduced prior to spinning (fibers) or fabrication. This approach requires that the additive be stable under the conditions of spinning or fabrication, and that it be uniformly dispersed and retained in the polymer fluid during processing in the amount needed to impart the desired level of flame resistance. In spite of these critical limitations, this approach is probably the most widely used for plastics (polyester resins, epoxy resins, etc.) and foams (polyurethanes). In the case of fibers, this approach has been used successfully

for regenerated cellulose fibers (rayon), and for acetate and triacetate fibers.

(3) *Graft copolymerization* of flame-retardant monomers onto a preformed polymer or fiber is a conceptually attractive approach to modification with flame retardants. It has been investigated extensively, and is reportedly approaching commercial development for regenerated cellulose (rayon) fibers in Europe. While commercialization has not been reported, the flexibility of the approach and the multitude of disclosures in the technical literature suggest that this route may become more important in the future.

(4) *Finishing* with flame-retardant compounds or systems is very important in the case of textiles, which may be manufactured from one or more fibers. This is also obviously the only possible approach for the chemical modification of natural polymers (wood, cotton, and wool) with flame retardants. Flame-retardant finishes may be nondurable (removed in washing or cleaning) or durable (retained in washing or cleaning). In the latter instance, they must be insolubilized after applicaion, either by reaction with the substrate or by polymerization *in situ*. Treatment with durable flame-retardant finishes has found successful commercial application for flame-resistant cotton fabrics.

Finishing of textiles (fabrics) in principle would include graft copolymerization with flame-retardant monomers, see (3) above, carried out as a topical treatment at the end of the fabric manufacturing process. The advantage of finishing as an approach is that it is versatile, flexible, and often relatively easy to implement in conventional equipment. However, the amounts of finish needed are frequently large enough to impair product properties, and the approach is by no means universal.

(5) The use of flame-retardant *coatings* to protect flammable substrates is an old approach to flame retardation, still widely practiced (e.g., marine

TABLE V

Examples of Flame-Retardant Compounds Proposed as Monomers for Graft Copolymer Preparation

Compound(s)	References	Manufacturer
$CH_2 = CHP(=O)(OCH_2CH_2Cl)_2$	USP 3,822,327 (1974)	Stauffer Chemical Company
$CH_2 = CHBr$, $CH_2 = CHCl$	----	Ethyl Corporation
$BrCH_2CHBrCH_2OC(=O)-CH = CH_2$	USP 2,993,033	Great Lakes Chemical Corporation
$CH_2 = CHC(=O)OCH_2P(O)(OR)_2$	German Patent 1,100,287 (1961) Chem. Abst. 56, 7520 (1962) Chem. Abst. 63, 13420 (1965)	

paints). Flame-retardant coating formulations may be of the "conventional" (i.e., nonintumescent) or intumescent type, the latter type being more effective, technologically advanced, and costly. In flame-retardant coatings, aging and weathering characteristics are critical, and not easily attained.

Examples of flame-retardant compounds of each of the types outlined above are summarized in Tables III–VII.

TABLE VI
Examples of Flame-Retardant Compounds Used as Durable Finishes on Fabrics

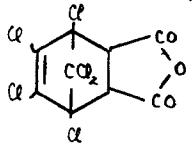
Compound(s)	Used in Fiber (polymer)	Application	Reference
$[(HOCH_2)_4P^+]Cl^-$ + $-NH_2$ containing coreactants	Cellulose	Cotton	Lyons, 1970a, pp. 189-208.
$(CH_3O)_2P(=O)CH_2CH_2CONHCH_2OH$	Cellulose	Cotton	Aenishanslin, Text. Res. J. 39, 375 (1969), USP3,423,369(1969).
$\left[OP(CH=CH_2)-OCH_2CH_2\right]_n$	Cellulose	Cotton	Eisenberg and Weil, Text.Chem. Col. 6, 180 (1974), USP3,695,925(1972).
$(BrCH_2CHBrCH_2O)_3P=O$	Polyethylene-terephthalate	Polyester	
Titanium and Zirconium complexes	Keratin	Wool	British Patent 1,372,694 (1974), Lewin et al., 1975, pp. 161-175.

D. Evaluation of Flame Retardants

It has been pointed out (Sec. IIIA) that this review will not deal with the complex subject of flammability testing, nor with the correlation of laboratory test results with fire hazards. However, in the laboratory development of flame-retardant compounds or systems, a meaningful evaluation of flame-retardant effectiveness and trends is essential to progress. Visual observations of burning behavior are useful, but generally lack the means for quantitative expression and precision. Many laboratory techniques for evaluating specific products (e.g., fabrics) or specific flammability parameters (e.g., rate of flame spread) in specified configurations are documented in the technical literature.

TABLE VII

Examples of Flame-Retardant Compounds Used in Coatings

Compound(s)	Coating type	Reference
Chlorendic anhydride 	Alkyd	Cleaver, 1973.
Chlorinated paraffin and Antimony oxide	Alkyd	Touval, 1972.
Phosphonic acid or Phosphates and polyol	Intumescent	F.B.Clarke and J. W. Lyons JACS 88, 4401 (1966), Vandersall, 1971.

However, the most important tool for the laboratory evaluation of flammability in polymers is the limiting oxygen index test developed at the General Electric Company (Fenimore and Martin, 1966) for polymer sticks, and since then, adapted to a wide variety of polymeric materials and compositions, and to liquid fuels.

The oxygen index of a material is the minimum percentage of oxygen in an oxygen-nitrogen atmosphere required to sustain combustion of the material after ignition:

$$\text{Oxygen Index (OI)} = \frac{[O_2]}{[O_2] + [N_2]} \times 100$$

The test is generally carried out with the sample burning downward in a candlelike manner, producing a gaseous diffusion flame above the polymer surface (Martin, 1968). Several recent reviews of the oxygen index test theory and uses (Nelson et al., 1975; Kanury, 1975; Fenimore, 1975) provide extensive information on this subject, which is considered of great importance. Oxygen index values for fibers and plastics are summarized in Tables VIII and IX. These may not be identical with values reported in technical publications for specific compositions, because of variations in the specific composition, sample preparation or geometry, or because of difficulties (melting and dripping) encountered in measuring the oxygen index of thermoplastic samples. Allowing for such variations, the oxygen index method provides a research tool of exceptional consistency and reproducibility.

TABLE VIII

Oxygen Index of Fabrics Made from Spun Yarns[a]

Fiber (type)	Oxygen Index [$\%O_2$]
Acrylic (ACRILAN)	18.2
Cellulose Triacetate (ARNEL)	18.4
Cellulose Acetate	18.6
Polypropylene	18.6
Rayon (regenerated cellulose)	19.7
Cotton (greige)	20.1
Nylon (6,6)	20.1
Polyester (DACRON)	20.6
Wool (dry cleaned)	25.2
Modacrylic (DYNEL)	26.7
Polyvinylchloride (RHOVYL)	27.1
Aramid (NOMEX)	28.2

[a]Fabric weight 4.8–7.0 oz/yd^2. Source: Tesoro and Meiser (1970).

TABLE IX

Oxygen Index of Plastics[a]

Polymer (type)	Oxygen Index [$\%\ O_2$]
Polyacetal	15.0
Poly(methyl methacrylate)	17.3
Polypropylene	17.5
Polystyrene	17.8
Cellulose (filter paper)	18.2
ABS Resin	18.8
Cellulose acetate	19.0
Polyethylene terephthalate	20.0
Polyaryl ether/polystyrene (NORYL)	24.3
Nylon (6,6)	24.3
Polycarbonate	24.9
Polyphenylene oxide	30.0
Polysulfone	38.0
Polyphenylene sulfide	> 40.0
polyvinyl chloride	40.3
polyvinylidene chloride	60.0
Polytetrafluoroethylene	95.0

[a]Sources: Fenimore and Martin (1966), Isaacs (1970), Imhof and Stueben (1973).

VI. PROBLEMS IN POLYMER MODIFICATION WITH FLAME RETARDANTS

The principles and approaches discussed in Sec. V have indicated some general problems associated with the use of flame retardants in polymers, and some formidable technological obstacles which must be overcome. The magnitude of specific problems and obstacles depends on the end use, the level of fire resistance required, and polymer substrate considered. The most important problems are briefly discussed below.

A. Incorporation of Effective Amounts

As a first approximation, modification of polymers to impart flame resistance requires larger amounts of the modifying reagent (comonomer, additive, etc.) than modifications designed to impart other desirable properties. This fact has important consequences, since the effect of the added material (flame retardant) on polymer properties is considerable, generally negative, and difficult to overcome. The effect on polymer properties may cause the polymer to fail one or more critical requirements, either in product manufacture or in use. The problem is compounded by the inadequacy of laboratory test methods by which flame-retardant effectiveness of modifying reagents can be evaluated. The minimum amount of flame retardant required cannot be established with precision and the effect on polymer flammability can be defined only in relative terms, with reference to carefully specified test procedures. The incorporation of effective amounts of flame retardants in polymers without impairing polymer properties is an extremely difficult problem.

B. Retention in Use

Assuming that an effective flame retardant and a viable approach to the modification of a given polymer have been identified, it is necessary to establish that flame-retardant effectiveness will not be lost during the useful life of the polymer. This entails evaluation of the effect of environmental conditions which the product is likely to encounter in use (e.g., light, temperature, abrasion, etc.) and of aging. For some products (e.g., apparel textiles) this also includes the evaluation of durability to laundering (up to 50 times or more) and dry cleaning.

C. Environmental

Effective flame-retardant compounds that can be retained adequately in polymeric substrates in use are generally organic compounds of phosphorus and halogen. These may be structures which possess physiological activity, and may pose problems of several kinds. The compounds must be safely handled in industry (occupational health), and must not accumulate in the environment. They must not pose a health hazard in use, and should not

yield abnormally toxic degradation products when the modified polymers burn. These requirements are not clearly defined, and many compounds now in use may have to be replaced as hazards resulting from their use are identified and as new regulations are issued. The status of the controversy on environmental pollution by fire-retarded polymeric materials is currently under review. Studies of mutagenic and carcinogenic effects of a potentially effective flame retardant (McCann et al., 1975), of toxic effects of flame retardants to fish (Gutenmann and Lisk, 1975), and physiological effects of selected flame-resistant fabrics (St. John et al., 1976) are illustrative of ongoing efforts to define the magnitude of the problem.

D. Cost

The cost of chemical modification of a given polymer with flame retardants includes many components, including chemical cost of added flame retardant, processing cost of modification, cost of adjustments in manufacturing processes for modified polymer, increased fabrication cost of products in which the modified polymer is used, and costs of quality control (flame resistance).

Inevitably, consumers must pay higher prices for flame-resistant products. The costs are high initially, but decrease with improved technology and increased use. Since most flame-resistant polymers in use at this time have neither "matured' technologically, nor reached maximum volume usage, current economic appraisals are tentative.

E. Flammability, Smoke Evolution, and Toxicity of Combustion Products

Modification of polymers with flame-retardant compounds is designed to decrease the probability of ignition and of sustained combustion on exposure to heat. This is an important aspect of fire hazard. Other aspects include smoke evolution (which can impair visibility and egress), and the formation of degradation products, either particulate or gaseous, which may be toxic or lethal. Evolution of smoke and toxic degradation products from materials exposed to fire is a complex function of composition and of the conditions of burning: the presence of flame retardants in the material may, in some instances, increase smoke and toxicity of degradation product, but generalizations are not possible on the basis of knowledge available at this time. Furthermore, laboratory tests for the evaluation of smoke evolution and of toxicity of degradation products are of limited value in predicting the behavior of the materials under realistic use conditions. The state of the art must be advanced significantly before the interrelationship of flame retardation, smoke evolution, and toxicity can be discussed.

VII. POLYMERS AND APPLICATIONS

Modification of polymers with flame retardants can be discussed with reference to the chemical structure of the polymer to be modified (e.g., cellu-

lose, polyacrylonitrile, etc.), the major application of the polymers (e.g., fibers, plastics, foams, etc.), or the chemistry of added flame retardants (e.g., phosphorus compounds, halogen compounds, etc.). Each method of classification has advantages. Emphasis on polymer science and engineering requires some combination of the first and second breakdown of the subject matter. The matrix given in Table X includes the major subject matter of this review (fibers, thermoplastic resins, and foams), but does not include thermosetting resins, elastomers, and coatings which are treated only briefly in the article.

TABLE X

	Wood	Fibers (Textile)	Plastics (Thermoplastic)	Cellular Plastics (Foams)
Cellulose	•	•		
Cellulose esters		•	•	
Polypeptide		•		
Polyamide		•	•	
Polyester		•	•	
Acrylic		•	•	
Polyvinyl Chloride		•	•	•
Polyolefins		•	•	•
Polyurethanes		•		•
Polystyrene			•	•
Polyacetal			•	
Polycarbonate			•	

Generally speaking, thermosetting resins are less likely to require modification with flame retardants than thermoplastics, and the state of the art is accordingly less advanced. Flammability and flame retardation of elastomers have not been studied extensively to date. In the case of coatings, the subject requires consideration of a highly specialized technology, in which knowledge of coating formulations is an essential component: coatings of reduced flammability would be treated as special formulations rather than as modified polymers.

There are numerous uses of polymeric materials where modification of the polymers with flame retardants is of interest and concern as improved fire safety becomes increasingly important. In some instances, flame retardants must be used to meet existing flammability standards (federal, state, or local); in others, they are used to comply with performance requirements specified by the user; in other instances, the use of flame retardants is contemplated for

TABLE XI

Polymeric Material	Application	Regulations and Standards for Flammability (1976) In effect	Planned
Wood	1. Structural		
	2. Furnishings		
Fibers	1. Apparel	•	•
	2. Furnishings		
	general		•
	institutional	•	•
	aircraft	•	•
	ground transp.		•
	3. Tents	•	•
Plastics	1. Building		•
	2. Furniture		
	3. Aircraft	•	•
	4. Ground Transportation		
	5. Recreational		
Foams	1. Furnishings	•	•
	2. Building	•	•
	3. Aircraft	•	•
	4. Ground Transportation		•

future developments. Table XI summarizes major applications of polymeric materials for which modification with flame retardant is now required, and/or expected to become an important part of future technology. The building industry, and the transportation industry (aircraft and ground transportation) will probably consume large volumes of flame-resistant (modified) polymers as new flammability standards and regulations are promulgated.

VIII. WOOD, BOARD, AND PAPER

The importance of wood and wood-based products (insulation board, hardboard, and particle board) in our environment is obvious. Similarly, enormous quantities of paper and paperlike products are consumed daily, frequently in situations where fire safety considerations are important. Wood and paper products consist essentially of cellulose, as do the cellulosic textile fibers to be discussed in a later section of this review. Thus, flame-retardant compounds that inhibit flammability of cellulose are, in principle, effective for wood, paper, and cellulosic textiles. It is clear, however, that flammability

and performance requirements, durability of flame resistance, critical side effects, and economics are vastly different for these products. The subject of flame retardants for cellulose must be divided into its logical components; namely, wood and wood-based products, paper products, and cellulosic textiles.

A. Wood Products

Modification of wood and wood-based products with flame retardants aims at preventing ignition and at reducing the rate of flame spread if ignition occurs. It can be approached either by impregnation of the substrate with flame retardants, or by surface coatings. The former method has a long history, dating back to the first century B.C., when alum and vinegar solutions were used as fire-retardant treatments for wood! Nevertheless, only about six million cubic feet of wood and plywood were treated with flame retardants in 1972—less than 0.1% of the annual production! The cost of treatment has been the principal reason for such limited use. Although the flame-retardant chemicals are relatively inexpensive, the processing cost is high and the treatment increases the cost of the wood or wood products by 50–100%. The chemicals and treatment processes used commercially (Eickner, 1966) have been developed primarily from empirical knowledge and pragmatic observations over the years. Recent research on the manner in which flame-retardant compounds alter pyrolysis and combustion processes in wood cellulose now provides a conceptual framework for established approaches and for new developments as well.

It is now generally accepted that flame-retardant chemicals that are effective for cellulose (specifically wood) alter the course of thermal degradation reactions in the solid phase, increasing the amount of char, water, and carbon dioxide formed at the expense of combustible degradation products (organic volatiles—tars and gases). Evidence for this mechanism of effectiveness has been obtained primarily by thermal methods of analysis. A review of the literature on thermal degradation of wood components (Beall and Eickner, 1970) coupled with the results of investigations carried out on wood treated with flame retardants (Tang and Eickner, 1968; Lyons, 1970a) have established that effective flame retardants facilitate degradation reactions. Volatile degradation products from treated wood provide less energy on combustion than the same weight of volatiles from untreated wood, while the char yield is significantly increased. Thermal data showing the effect of additives in alpha-cellulose (Tang and Neil, 1964) are shown in Table XII, and are indicative of the approaches used for imparting flame resistance to wood, involving primarily inorganic salts. A summary of inorganic salts which have been found effective is presented in Table XIII.

Eickner (1966) points out that these inorganic salts are generally used in mixtures containing several compounds (e.g., 10 parts diammonium phosphate + 60 parts ammonium sulfate + 10 parts borax + 20 parts boric acid = "Minalith formulation"). Aqueous solutions containing 12–15%

TABLE XII

Thermal Data for α-Cellulose[a]

Additive	Activation energy of pyrolysis Kcal/mole	Heat of pyrolysis cal/g	Max rate of heat generation cal/g/min
None	33-35	88	870
2% $Na_2B_4O_7 \cdot 10\ H_2O$	30-32	58	730
2% $AlCl_3 \cdot 6H_2O$	33-33.5	57	665
2% $KHCO_3$	19-21	72	588
2% $NH_4H_2PO_4$	17-19	78	635
8% $NH_4H_2PO_4$	---	64	498

[a]After Tang and Neil, 1964.
[b]First stage, zero to first order.

concentrations of the flame-retardant salts are used for pressure impregnation of lumber or plywood, aiming for a dry-salt retention of 2.5–3 lb/ft^3 for plywood or 2-in. lumber (and decreasing amounts for thicker lumber).

Similar formulations can be used for the treatment of fiber board and hardboards. The pulp may be treated before sheet formation, or the wet pressed mat may be treated before drying. Hardboards have also been treated by pressure impregnation after hot pressing. Related processes have been disclosed for particle board (Lewin et al., 1975).

Approaches for chemical modification of wood with organic and/or reactive flame-retardant compounds include (1) impregnation from emulsions of organic phosphates in combination with oil-borne preservatives (Gooch et al., 1959); (2) impregnation from solvent solution of organic compounds of phosphorus and halogen (Lyons, 1970a; Lewin et al., 1975); (3) impregnation with (unsaturated) organophosphorus monomers polymerized *in situ* by radiation (Raff et al., 1966); (4) bromination of lignin to produce bromolignin as the effective flame retardant (Lewin et al., 1965).

To date, these approaches are developmental at best, and no commercial utilization has been reported, presumably due to the high cost of the chemicals and/or processes needed. Modification by impregnation from aqueous solutions of reactive flame-retardant compounds, followed by *in situ* insolubilization, either by reaction with cellulose hydroxyls or by polymerization, is not practical for the treatment of wood (even though it is the method of choice for the treatment of cellulosic textiles). Since insolubilization of the reactive system is generally brought about by heat-curing, the thickness of the wood substrate prevents the rapid uniform temperature distribution which is readily attained in the case of thin sheets such as textiles.

Wood and wood-based products properly treated with fire-retardant formu-

TABLE XIII

Compound(s)	References
$NH_4H_2PO_4$ $(NH_4)_2HPO_4$ $(NH_4)_2SO_4$ with and without addition of urea or other components	R. H. Mann et al., Proc. Am. Wood Preservers Assoc. (1944), 261, T. R. Truax et al., Proc. Am. Wood Preservers Assoc. (1933), 107.
$Na_2B_4O_7 + H_2BO_3$	G. M. Hunt et al., Proc. Am. Wood Preservers Assoc. (1932), 71.
$ZnCl_2$ + $Na_2Cr_2O_7 \cdot 2H_2O$	H. W. Angell, Proc. Forest Products Res. Soc. 5, 107 (1951).
$ZnO; H_3PO_4$ + $CuSO_4$; $K_2Cr_2O_7$	D. F. McCarthy et al., J. Inst. Wood Sci. 6 (1), 24 (1972).

lations have decreased rates of surface flame spread (ASTM Test for surface burning characteristics of building materials E-84-61) and are self-extinguishing (flaming and glowing) when the external source of heat is removed. The fire-retardant treatments also reduce the maximum rate of heat release. The amount of smoke produced by burning the treated wood depends greatly on the chemicals included in the formulation and on the fire exposure conditions. Information about the effects of treatment on the toxicity of the pyrolysis and combustion products is very limited. Untreated wood produces some toxic carbon monoxide and irritant gases and vapors, such as acetic acid, formaldehyde, glucosans, and phenols in burning. The use of fire retardants results in a reduced percentage of tars and vapors and in a greater percentage of wood retained as a charcoal residue.

In modifying wood by chemical treatment, the influence on many properties must be considered, including the effect of added flame retardants on

strength, durability, hygroscopicity, corrosiveness, painting, gluing, and machining characteristics. Reduced performance in some of these characteristics (in addition to the cost of fire-retardant treatment) has limited the use of wood-based products treated with fire retardants.

Many of the chemicals used as fire retardants are water-soluble inorganic salts, easily leached from the wood: therefore, the treatments are primarily limited to interior uses.

Furthermore, some chemicals used in fire-retardant formulations are hygroscopic, and as water is absorbed, droplets may come to the surface and drop from the treated substrate, with consequent loss of fire retardant. Many of the inorganic salts used as fire retardants are corrosive to certain metals and alloys. Formulations can be balanced and neutralized, and commercial corrosion inhibitors added so that this does not pose a problem. However, if treated wood is exposed for long periods at high relative humidities, moisture and chemicals may be exuded on the metals, and produce various forms of electrolytic corrosion, which the inhibitors may not be able to control.

The processing and addition of fire-retardant chemicals to wood decrease the modulus of elasticity by 5–10%, and the modulus of rupture by 10–20% as compared to untreated controls. There is also a decrease in resistance to impact loading.

Additional problems to be considered in the evaluation of wood treated with fire retardants are the possible abrasive effect of the salts present on cutting tools (machining); the effect of the additive on adhesive bonding of structural components (gluing), and of surface coatings (painting).

B. Paper Products

Flame retardants recommended for paper and paper products have closely paralleled those suggested for other forms of cellulose, particularly wood, since the beginning of this century. The most commonly used materials are ammonium sulfate and ammonium phosphates, with or without boric acid, but a large number of more sophisticated retardants have been suggested for various specialty applications (Lyons, 1970a). There are several modes of adding flame retardants to paper products, depending on the solubility of the compounds, on the paper product involved, and on cost considerations. The selection and application of specific flame retardants to paper products as a function of the inherent specialized technology are considered beyond the scope of this review.

IX. FIBERS AND FABRICS

A. Cellulose (Cotton and Rayon)

1. Introduction

There are important historical and economic reasons for the fact that the

science and technology of flame retardants for cellulose fibers are far more advanced than for other fibers and polymers: until perhaps 25 years ago, an overwhelming proportion of all textiles used was made of cellulosic fibers, and until recently the research challenge of reducing flammability in polymers has focused primarily on wood (Sec. VIII) and on cotton as the substrates. The classic textbooks of the 1940s on the subject of flame retardants for fabrics (Little, 1947; Ramsbottom, 1947) thus cover cellulosics exclusively.

Extensive research on the thermal degradation of cellulose (Shafizadeh, 1968) and on the manner in which added flame retardants alter the course of degradation reactions, has led to a partial elucidation of the mechanism of fire-retardant action by Lewis acids. The principal role of acid or acid-forming flame retardants in cellulose is to enhance dehydration and char formation in the condensed phase, suppressing the formation of combustible volatiles in the thermal degradation process. This theory, first postulated many years ago (Schuyten et al., 1955), has been supported by experimental evidence obtained on many cellulosic substrates and flame-retardant compounds. Phosphorus acids are particularly efficient in catalyzing cellulose dehydration, and phosphorus-containing flame retardants have been studied most extensively. In the case of natural cellulosic fibers, modification with flame-retardant compounds has been accomplished almost exclusively by finishing of fabrics. In the case of regenerated cellulose fibers, the most important approach to modification has been the incorporation of flame-retardant additives in the spinning fluid (see Sec. VC).

2. Cotton Fabrics

Flame-retardant finishes for cotton fabrics have been reviewed in books (Little, 1947; Lyons, 1970a; Lewin et al., 1975), encyclopaedia articles (Drake, 1966, 1971), and in a large number of other publications. Literally hundreds of formulations, and dozens of different compounds have been proposed. Milestones of the evolution from simple processes involving deposition of inorganic salts (readily removed by water) to sophisticated modifications of the cellulose molecule and/or *in situ* polymerization of appropriate monomers are summarized in Table XIV. The most significant relevant references are indicated at the end of Table XIV.

The definition of "ideal" requirements for durable flame retardants for cotton fabrics was perfectly formulated by Sir William Perkins in 1912 (Ref. 2 in Table XIV; see also Lyons, 1970a). Perkins' attempt to precipitate a water-soluble flame-retardant compound (stannic oxide) *in situ* to attain durability to laundering remains an important conceptual milestone in the evolution of current technology. Methods for testing flame resistance of treated cottons were crude and pragmatic. They were not formalized until interest in the treatments was stimulated by the military in the late 1930s. During the period of World War II, a vertical flammability test was developed for fabrics treated with flame retardants (ASTM-D-626; AATCC 34; Federal Spec.

TABLE XIV

History of Flame Retardants for Cellulosic Fabrics

Year	Compounds	Applications	Ref.
1821	Mixtures of ammonium phosphate, ammonium chloride and borax	Linen and jute fabrics	(1)
1912	Sodium stannate followed by ammonium sulfate to precipitate stannic oxide in situ	Cotton flannel	(2)
~1940	Chlorinated paraffin and antimony oxide	Canvas for military tentage "FWWMR" finish	(3)
~1948	Phosphorylation of cotton (urea-phosphate)	Cotton fabrics for apparel	(4)
	Titanium oxychloride and antimony oxychloride	Cotton fabrics "ERIFON" finish	(5)
1956-1958	Trisaziridinyl phosphine oxide (APO) and Tetrakis hydroxymethyl phosphonium chloride (THPC) developed at USDA as components of durable finishing systems	All types of cotton fabrics	(6)
1968-1969	N-methylol dimethyl phosphonopropionamide (Pyrovatex CP)	All types of cotton fabrics	(7)
1969-1970	N,N',N" Trimethyl phosphoramide with trimethylol melamine (MCC 100/200/300)	All types of cotton fabrics	(8)
1971	Vinyl phosphonate oligomer (Fyrol 76) copolymerized with N-methylol acrylamide	All types of cotton fabrics	(9)
1974-1975	Methyl phosphonic diamide, chloromethyl phosphonic diamide	All types of cotton fabrics	(10)

[1]Gaylussac (1821).
[2]Perkins (1913a, b).
[3]Chase (1943) and USP. 2,299,612.
[4]Davis et al. (1949); Nuessle (1956); and USP 2,935,471 (1960) to Dupont.
[5]Gulledge and Seidel (1950).
[6]Reeves and Guthrie (1956); Drake and Guthrie (1959); see also Lyons (1970a),pp. 174–178 and 189–208.
[7]Aenishänslin et al. (1968, 1969); and USP 3,423,369 (1969) to CIBA, Ltd.
[8]USP 3,632,297 and 3,681,060 (1972) to J.P. Stevens.
[9]Eisenberg and Weil (1974).
[10]Tesoro, Valko, and Olds (1976).

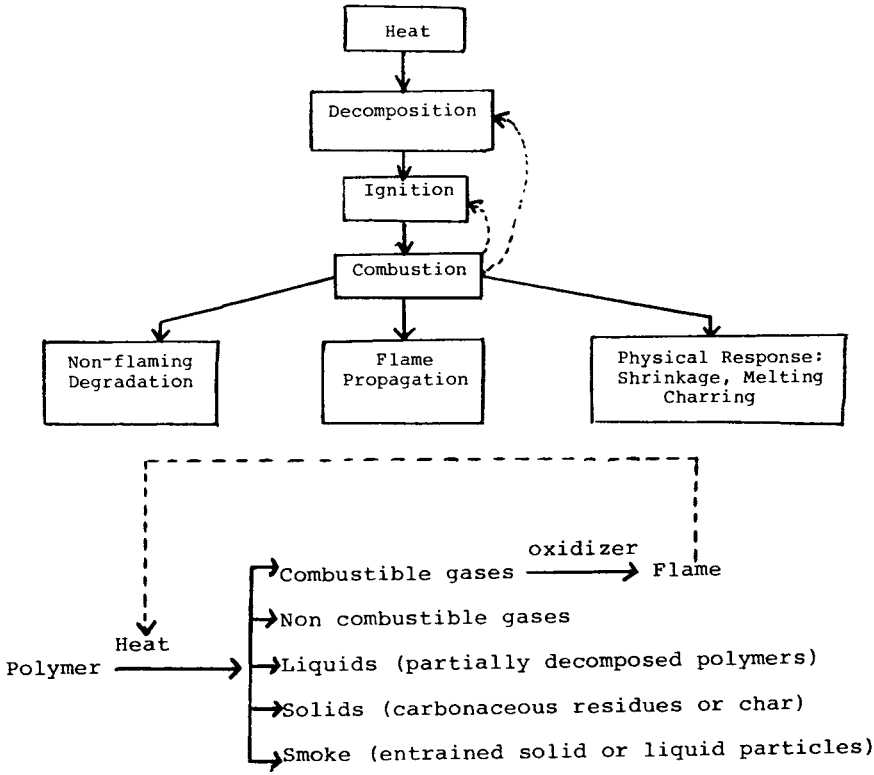


Fig. 1. Thermal degradation, ignition, and combustion processes for organic polymers represented by general sequences. Thermally induced decomposition clearly precedes ignition.

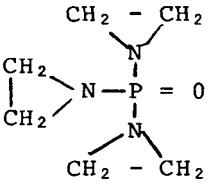
5902, 5903) and widely adopted as a measure of flame resistance by workers in the field. Fabrics which are self-extinguishing in this test were designated as "flame resistant" in publications from about 1940 until about 1970, when modifications of this test became a part of federal standards (e.g., DOC-FF-3–71). In the late 1930s and early 1940s, flame-retardant finishes based on chlorinated paraffins and antimony oxide in conjunction with resin binders were developed for tent fabrics (Ref. 3 in Table XIV). Large amounts of finish (up to 60% solids applied based on fabric weight) were used, impairing the flexibility and air permeability of the treated fabrics. However, the finish succeeded in combining flame resistance, water and mildew resistance for a critically important application, and 700 million yards of fabric were processed with it during World War II. Clearly, the development was not applicable to apparel fabrics.

Attempts to obtain durable flame resistance in cotton by chemical modification of the cellulose molecule were made in the late 1940s. Work on phosphorylation of cellulose in the presence of large amounts of urea or other basic compounds to prevent acid degradation and depolymerization of the poly-

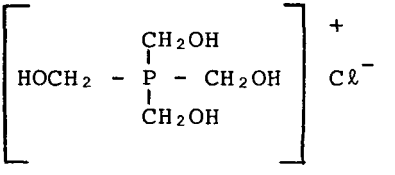
mer (Ref. 4 in Table XIV) led to a process which was used on a commercial scale for a time. However, the phosphate ester linkage introduced into the cellulose is not sufficiently stable to hydrolysis to withstand repeated laundering and the presence of ion exchange sites in the modified cotton leads to replacement of NH_4^+ by metal cations with loss of flame resistance.

Work on the reaction of cotton with titanium oxychloride and antimony oxychloride (Ref. 5 in Table XIV) enjoyed a brief period of intense interest in the 1950s and was presumably abandoned due to practical difficulties of handling in the mills.

The development of "modern," truly wash-resistant, or durable flame-retardant finishes for cotton fabrics began in the late 1950s with the USDA investigations focusing on the reactions of two organophosphorus molecules, APO and THPC (see below)



APO



THPC

with cellulose, with coreactants, and with each other (Ref. 6 in Table XIV). Self-extinguishing cotton fabrics of reasonable properties found to withstand a large number of wash cycles and exposures were obtained for the first time. During this period, two important working hypotheses evolved: that about 3% insolubilized phosphorus was needed to attain satisfactory flame resistance (self-extinguishing behavior in the AATCC vertical test) in most cotton fabrics; and that insolubilization of the phosphorus could be attained either by reaction with cellulose OH groups (e.g., phosphorylation, APO, etc.), or by *in situ* polymerization of appropriate monomer systems (e.g., THPC with nitrogen-containing comonomers such as urea, NH_3, etc.). Subsequent developments confirmed and refined these working hypotheses. Finishes based on THPC chemistry have been produced commercially for a decade, and remain important. Finishes based on APO chemistry have been abandoned primarily because of toxicity and/or suspected carcinogenic properties of the reagent (APO) and its precursor (ethylene imine).

Flame-resistant cotton fabrics produced commercially in the 1970s are made by finishing with systems summarized in Table XV (reference numbers from Table XIV are repeated). Others have been considered, or are currently under consideration: the *N,N,'N''*-trimethyl phosphoramide system (Ref. 8 in Table XIV) has reportedly been shelved, and the methyl phosphonic diamide system (Ref. 10 in Table XIV) has not reached commercial status.

TABLE XV

Commercial Chemicals for Flame-Retardant Finishing of Cotton Fabrics

Organophosphorus Compound	Coreactant(s) Required	Insolubilization (Ref)	% Finish Applied	Insol.	%P Insol.[a]
$(CH_3O)_2\overset{O}{\overset{\|\|}{P}}-CH_2CH_2CONHCH_2OH$	---	Reaction with cellulose OH[b]	30-40	20-30	2-3
$[(HOCH_2)_4P]^+ X^-$ X = Cℓ, OH, etc.	NH_3, NH_2CONH_2, etc.	In situ polycondensation[c]	30-40	25-35	3-5
$\left\{O-\overset{O}{\overset{\|\|}{P}}(CH=CH_2)-OCH_2CH_2\right\}$	$CH_2=CHCONHCH_2OH$	In situ polyaddition (free radical polymerization)[d]	25-35	20-30	2-4

[a]For SE behavior in vertical flammability tests.
[b]Aenishänslin et al. (1968, 1969) and USP 3,423,369 (1969) to CIBA, Ltd.
[c]Reeves and Guthrie (1956); Drake and Guthrie (1959). See also Lyons (1970a).
[d]Eisenberg and Weil (1974).

TABLE XVI

Experimental Chemicals for Flame-Retardant Finishing of Cotton Fabrics

Organophosphorus Compound (%P)	Coreactant(s) Required	Insolubilization Mechanism	% Finish Insolubilized[a]	% P Insol.[a]
$P(NH_2)_3$ ‖ O (32.5)	$NH_4SO_3NH_2$ + bis methoxy-methyl uron	Reaction with cellulose OH[b]	15-20	2.0-2.2 (+ 2% S)
$ClCH_2P(=O)[N(CH_2)_2CH_2]_2$ (17.2)	---	Reaction with cellulose OH[c]	8-16	2.0-3.1
$CH_3P(=O)(NH_2)_2$ (33.0)	---	Reaction with cellulose OH[d]	7-14	1.8-3.6

[a]For SE behavior in vertical flammability tests.
[b]Lewin et al. (1973).
[c]Tesoro, Olds, and Babb (1974).
[d]Tesoro, Valko, and Olds (1976).

Table XVI summarizes experimental chemicals of continuing interest at this time.

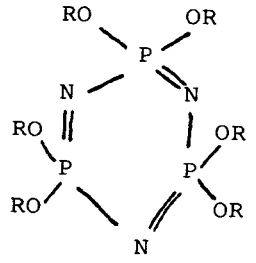
3. Other Cellulosic Fabrics

In principle, approaches used for finishing of cotton fabrics are applicable to other cellulosics (rayon, linen, jute, etc.). In fact, the properties of different fibers and fabrics require extensive modifications in the technology of the process, and in the amounts of flame-retardant finish needed to attain a specified level of flame resistance. A discussion of these differences from the viewpoint of textile technology is beyond the scope of this review. Suffice it to say that commercial production of flame-resistant 100% cellulosic fabrics by finishing has been limited to cotton, and some specific rayon fabrics (e.g., draperies).

4. Regenerated Cellulose (Rayon) Fibers

The incorporation of flame-retardant additives in the fiber-spinning process is a problem of considerable complexity. The technical accomplishment of having developed and produced flame-resistant rayon fiber on a commercial scale should not be underestimated. Whatever the commercial future of this product may hold, its development can be considered an important milestone in fiber technology.

Flame-resistant rayon fiber can be used to manufacture fabrics which are self-extinguishing in a vertical test. It has been made commercially by incorporating an alkoxyphosphazene in the spinning fluid (Fig. 3). The commercial fiber employs the *n*-propoxy compound (R = *n*-C_3H_7-) as the additive (Godfrey, 1970):



Other approaches in which the rayon fiber is modified by graft copolymerization reaction with a flame-retardant monomer prior to yarn manufacture (Krässig, 1970; Brickmann and Fäessinger, 1973) have been suggested, but have not reached commercial status to date.

Appreciable quantities of disposable nonwoven textile items are produced

from rayon. These are not generally laundered for re-use and if flame resistance is needed, the materials can be treated with water-soluble inorganic flame retardants such as diammonium phosphate or ammonium sulfamate in appropriate formulations.

B. Cellulose Acetate and Triacetate

Cellulose acetate and triacetate fibers, or cellulose ester fibers made by acetylation of natural cellulose, are thermoplastic. They melt at relatively low temperature (Mark et al., 1968), they ignite, and they can propagate the flame even though they drip while they continue to burn. The principal, or perhaps the only method used to attain fire resistance in cellulose acetate and triacetate fibers is the incorporation of a flame-retardant additive (specifically, 2,3 tris dibromopropyl phosphate) (LeBlanc et al., 1973) into the spinning solution before extrusion. The bromine-containing product (flame-resistant acetate) obtained is somewhat more resistant to ignition than the unmodified acetate. Above all, if ignited, the modified material tends to drip without sustaining flame propagation and it is rated as self-extinguishing in vertical tests *providing* it is not tested or used in conjunction with a nonthermoplastic material (e.g., thread). If a nonthermoplastic component is present in the system, it acts as a wick for the molten acetate or triacetate polymer and burning is sustained. In this case, the amount of flame-retardant additive commonly used in spinning (about 10% based on polymer weight) is not sufficient to impart flame resistance and self-extinguishing behavior. Larger amounts of additive, on the other hand, would impair fiber properties and therefore not be practical.

C. Wool and Protein Fibers

Although the unique chemical structure of wool and other protein fibers offers many reaction sites and possibilities for chemical modification, studies of flame retardants in wool have been limited in number and in scope. The reasons are clear, since wool consumption is a very small percentage of total fiber consumption and, furthermore, wool textiles are generally less flammable than those made from cotton, regenerated cellulose, or from most synthetic fibers.

While most wool fabrics would *not* be self-extinguishing in vertical flammability tests, wool has a relatively high oxygen index and it exhibits relatively low flammability in tests less stringent than the vertical test. Work designed to enhance the "natural" flame resistance of wool has been reviewed by Benisek (Benisek, 1972, 1973; Lewin et al., 1975) .

Modification of wool with flame retardants has been based on three approaches: (1) nondurable treatments, mainly inorganic borates or phosphates, applied to fabrics for specialized applications such as theater curtains or aircraft upholstery; (2) modifications of systems developed for cellulosics and based on THPC chemistry, primarily developed to meet aircraft uphol-

stery specifications; (3) durable treatments based on titanium and on zirconium complexes, developed primarily for carpet wool, so as to meet the requirements of the "pill test" (DOC-FF-1–70).

The last approach (which is specific to wool) consists, for example, of the application of titanium tetrachloride and potassium titanium oxalate in conjunction with an alpha hydroxy carboxylic acid such as citric acid. The metal complexes exhaust on to the fiber at the boil at low pH (below 3) to impart flame resistance. The effect depends on the conditions of treatment, but self-extinguishing fabrics of oxygen index greater than 30 can be obtained by this process, which is reportedly used commercially in the U.S. and in Europe.

The flammability of fibers from other natural proteins (silk, collagen) has apparently not been investigated, and modifications with flame retardants have not been reported for these fibers.

D. Polyester Fibers (Polyethylene Terephthalate)

1. Introduction

Interest in flame-resistant polyester fibers [polyethylene terephthalate fibers marketed under several trade names, including Dacron (E.I. du Pont), Fortrel (Celanese Fibers Marketing Co.), Kodel (Tennessee Eastman)], has been stimulated by the amendment to the Flammable Fabrics Act, which was signed into law in December 1967. This law made it clear that new flammability standards for textile products would be forthcoming, coinciding chronologically with a spectacular growth of polyester fibers in the market place, and with increasing consumer acceptance of products made from or containing these fibers. Several facts must be emphasized before summarizing the state of the art on the chemical modification of polyethylene terephthalate (PET) fibers with flame-retardant compounds.

(1) The history of research and development accomplishments for this application is short (dating back only to about 1968).

(2) Because of time pressures imposed by legislative action and standards (either actual or expected), short-range solutions to the problem have been emphasized, perhaps at the expense of fundamental or long-range research. The technology developed has been designed primarily to meet specific requirements or standards, and has been based largely on available knowledge rather than on the long-range investigation of proposed new concepts.

(3) The thermoplastic behavior of PET fibrous structures causes them to shrink away from ignition sources, melt, and drip in most tests. This can result in self-extinguishing behavior and provides a measure of flame resistance in use, as long as the presence of nonthermoplastic components in the system is avoided.

(4) Modification of PET with flame-retardant compounds may be designed to decrease flammability in products (and tests) where the melt-drip mechanism is operative (e.g., 100% PET) and reported effectiveness of flame

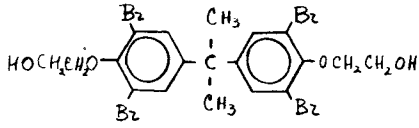
retardants may reflect also factors such as decreased melt viscosity or enhanced drip. In other instances, modification of PET with flame retardants may require that specified levels of flame resistance be attained in conjunction with nonthermoplastic fibers (e.g., polyester/cotton blends). In this case, the problems are far more complex.

(5) While melt-drip can lead to self-extinguishing behavior and flame resistance, the phenomenon also causes considerable difficulty in testing and evaluation, since results are dependent on sample orientation and test geometry even more importantly than in the case of nonthermoplastic materials. Flammability test results for thermopolastics *must* be qualified as to test method and conditions.

Approaches to the flame-retardant modification of PET fibers have included the use of bromine-containing or phosphorus-containing compounds as comonomers in the synthesis of a modified PET, or as additives in fiber spinning, and the finishing of PET fabrics with bromine-containing flame retardants. Recent reviews of these approaches are available (Lewin et al., 1975; Stepniczka, 1975b), and highlights are summarized below.

2. *Comonomers*

The use of flame-retardant comonomers in the synthesis of PET is technologically exacting. Even limited changes in the regularity of the linear chain, molecular weight, and physical properties of the fiber-forming polymer have profound effects on fiber spinning requirements, on the development of fiber structure (orientation and crystallinity) after spinning, and on fiber properties. In addition, the comonomers must be thermally stable to temperatures in excess of 250°C for several hours during the melt-copolymerization reaction. To date, only one copolymer flame-resistant polyester fiber has attained commercial status, namely Dacron 900F manufactured by du Pont (Bercaw, 1974). Reportedly, part of the ethylene glycol in the PET synthesis is replaced by the glycol (shown below) to attain a bromine content of 6% in the modified PET.



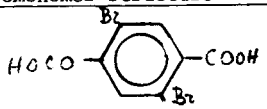
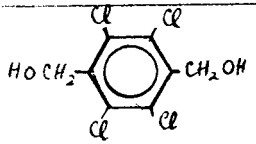
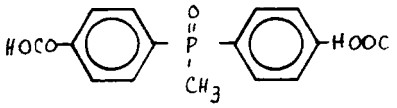
Other illustrative comonomers evaluated with varying degrees of depth are shown in Table XVII.

3. *Additives*

Compounds considered as flame-retardant additives in melt spinning of PET fibers must be stable at 260–300°C for sufficient time to allow proc-

TABLE XVII

Examples of Flame-Retardant Comonomers in Polyethylene Terephthalate Fibers

Comonomer Structure	Reference
	J. P. Nelson, 165th ACS Meeting, Dallas, Texas, April 1973.
	British Patent 1,248,835 (1971) (To Farbwerke Höechst A.G.).
	USP 2,646,420 (1953) (to du Pont).

essing of the polymer (spinning), and must be well dispersed in the polymer melt without detrimental effects on viscosity and flow. In addition, the compounds must satisfy other more general requirements (e.g., lack of toxicity, durability in use, effect on properties, etc.). Numerous compounds containing halogen and/or phosphorus have been evaluated. Halogen-containing additives have been tested also in combination with antimony oxide and other synergists. At this time, few among them have been considered for commercial development. Table XVIII summarizes structures documented as effective. It is important to point out, however, that much of the technology developed in this area by fiber manufacturers is considered proprietary, and not published. Furthermore, the state of the art is rapidly changing as new inventions are made and new patents issued.

4. *Fabric Finishes*

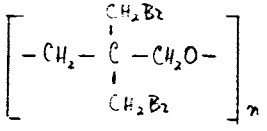
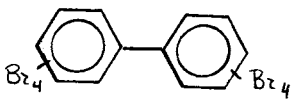
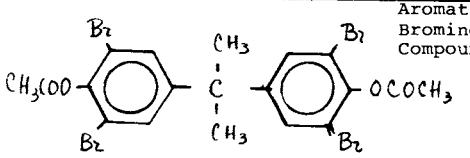
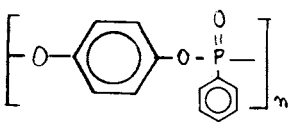
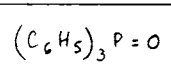
Topical treatment of 100% PET fabrics by diffusing flame-retardant compounds at elevated temperature have been developed in recent years and are used commercially. The most widely used compound in this application is tris 2,3 dibromopropyl phosphate:

$$(BrCH_2BrCH\ CH_2O)_3P = O$$

The patent literature documents many formulations and application procedures for this compound and for other bromine-containing flame retardants

TABLE XVIII

Examples of Flame-Retardant Additives for Polyethylene Terephthalate Fibers

Additive Structure	Type	Reference
	Aliphatic Bromine Compound	USP 3,645,962 (1972) [to Hercules Inc.].
	Aromatic Bromine Compound	Jap. Pat. 4,602,959 (1971) [to Celanese Corp.], Belgian Pat. 773,986 (1972) [to Dow Chemical Co.].
	Aromatic Bromine Compound	British Pat. 1,281,937 [to ICI].
	Phosphonate Oligomer	Jap. Pat. 4,739,154 (1972), 4,743,041 (1972), USP 3,719,727 (1973) [to Toyobo Co., Ltd.].
	Phosphine Oxide and Synergist	USP 3,681,281 (1972) [to Celanese Corp.], USP 3,629,365 (1971) [to Akzona Inc.], USP 3,660,350 (1972) [to MT Chemicals, Inc.].

suitable for finishing of 100% polyester fabrics (Stepniczka, 1975b). Generally, the requirements for the compounds include a high bromine content, and low vapor pressure at the temperature required for diffusion. Application of decabromodiphenyl oxide on the surface of fabrics in conjunction with binders has also been suggested as an alternative to the diffusion approach (Mischutin, 1975).

In addition to the commercial or semicommercial processes indicated above, experimental finishes for 100% PET have utilized the concepts of graft polymerization or *in situ* polymerization of phosphorus-containing vinyl monomers and of surface halogenation of the fibers. Specific examples of these approaches are given in the reviews cited (Lewin et al., 1975; Stepniczka, 1975b).

E. Polyamide Fibers (Nylons)

Nylon 6,6 and nylon 6 are commercially important polyamide fibers. Some

of the considerations discussed in Sec. IXD1 above for polyester fibers would apply to nylon fibers as well. For these also, the study of flammability behavior became important as a consequence of the 1967 law. Nylon fibers are also thermoplastic, and therefore subject to melting and dripping on exposure to elevated temperature. However, the principal end-uses for nylon fibers are different from those developed for PET fibers, and standards of performance properties, including flammability, are therefore different. Nylon is used primarily in 100% form (rather than in blends with natural fibers). Among the major uses for nylon fibers are carpets and rugs, where existing flammability standards can be met without chemical modification with flame retardants, and apparel categories (e.g., ladies' underwear) in which existing and expected flammability standards can also be met with unmodified nylon. Perhaps for these reasons, efforts towards the development of approaches to flame retardation in nylon fibers have been less intensive than in the case of PET fibers. These approaches have been reviewed in recent publications (Lewin et al., 1975; Stepniczka, 1973, 1975a; Gilleo, 1975), and they are based primarily on the use of additives in melt spinning, or on fabric finishing. There are, in fact, *no* documented means for improving the fire resistance of nylon fibers without serious drawbacks. One approach frequently cited and (probably) used for specialized commercial applications is based on the use of thiourea. Nylon fabrics can be finished with condensation products of thiourea and formaldehyde. This approach entails modification of the thermal degradation reactions of the polyamide, and probably enhanced dripping in the presence of thioruea (Douglas, 1957).

Phosphorus compounds are not effective flame retardants for nylon fibers. By promoting char formation, they inhibit dripping of molten nylon and seemingly increase flammability as compared to burning samples which are allowed to drip freely. Halogen compounds are not efficient: it is reasoned (Gilleo, 1975) that at low concentration they catalyze acid cleavage of amide groups and increase the rate at which combustible decomposition products are formed. At higher concentration, inhibition of free-radical reaction by halogen-containing species in the gas phase becomes overriding, and flammability is reduced, as indicated by significant increases in oxygen index. This assumption regarding the effect of halogen-containing flame retardants in nylon fibers is supported by observations reported for the oxygen index of nylon/polyvinylchloride fiber blends (Gilleo, 1975).

Metal compounds (particularly oxides, halides, and organic complexes of tin) have been claimed extensively in the patent literature as effective flame retardants for nylon, generally in conjunction with organic halogen compounds. Gilleo (1975) presents a review of relevant patents recently issued, but compounds specifically suitable for use in fibers are not identified.

In summary, nylon fabrics are frequently described as flame resistant. In small-scale flammability tests, the difference between melting point and ignition temperature of the nylon fibers allows dripping to occur, and in the absence of nonthermoplastic components in the system, nylon textiles do, in fact, exhibit "low" flammability.

On the other hand, chemical modification of nylon fibers with flame-retardant compounds poses unusual difficulties, and a commercially useful solution has not been developed to date.

F. Acrylic and Modacrylic Fibers

Acrylic fibers are defined by the Federal Trade Commission as containing "at least 85% by weight" acrylonitrile in the polymer chain. Modacrylic fibers, on the other hand, are those which contain "less than 85% but at least 35% by weight" acrylonitrile. Comonomers are generally used in the manufacture of acrylic fibers to improve specific properties. Modacrylic fibers were developed as an outgrowth of research on vinyl polymers, and not necessarily in a search for modification of acrylics with flame-retardant compounds. In fact, however, copolymerization of acrylonitrile with halogen-containing comonomers is the most important approach to the development of flame-resistant fibers based on polyacrylonitrile. When halogen-containing comonomers are included in amounts exceeding 15%, the fiber is classified as a "modacrylic."

The technology of modacrylic fibers and their history have been reviewed (Mark et al., 1968). Table XIX summarizes the status for halogen-containing, flame-resistant modacrylic fibers produced in the U.S.

TABLE XIX

Modacrylic Fibers Produced in the U.S.

Fiber Trade Name (Producer)	Comonomer (Probable)	Status	Reference
DYNEL (Union Carbide)	$CH_2 = CHCl$	Discontinued	F. Adams, Rayon and Synthetic Textiles 30(12),74 (1949), 31(1), 63 (1950).
VEREL (Tennessee Eastman)	$CH_2 = CHCl$ $CH_2 = Cl_2$	Commercial	H. W. Coover, Modern Textiles 37(11), 68 (1956).
SEF ACRILAN (Monsanto)	$CH_2 = CHCl$ $CH_2 = CHBr$	Commercial	A. A. Dunham, Proc. Symp. Text. Flamm., LeBlanc Research Corp., (1974), pp. 181-201.
ORLON FRL (du Pont)	N.A.	Developmental	J. R. Bercaw, (1974).

With the successful application of the concept of copolymerizing flame-retardant (halogen-containing) monomers with acrylonitrile in the manufacture of modacrylic fibers, other approaches to modification of acrylic fibers have not been emphasized. Research on the use of flame-retardant additives

for acrylic fibers has focused primarily on the evaluation of halogen and/or phosphorus-containing compounds (Nametz, 1970). Fabric finishes formulated from urea have been disclosed in the patent literature, but are believed to have little if any significance.

G. Polyvinyl Chloride and Polyvinylidene Chloride Fibers

These fibers manufactured from halogenated monomers are inherently flame resistant, and do not require chemical modification to attain self-extinguishing behavior under most conditions of testing. They are mentioned here because, as a class, they represent a unique example of fiber-forming polymers which are not thermally stable, but can be defined as inherently flame resistant. The history and properties of these fibers have been reviewed (Mark et al., 1968; Higginbotham, 1975) and utilization in flame-resistant textile products has also been discussed (Susani, 1974).

A comparison of the chlorine content of modacrylic fibers (34–36%), polyvinyl chloride fibers (57%), and polyvinylidene chloride fibers (~ 70%) has been reported (Collins, 1972). A bicomponent fiber made by cospinning polyvinyl chloride and polyvinyl alcohol is produced in Japan and exported to the U.S. under the trade name of Cordelan (Koshiro, 1973). The chlorine content of this fiber is comparable to that of the modacrylics, and flame resistance is at least as good.

H. Polyolefin Fibers

Polyethylene and polypropylene fibers (Mark et al., 1968) are hydrocarbons. Predictably, thermal degradation products of polyolefins ignite readily and burn with flaming drops. Chemical modification of hydrocarbon polymers with flame-retardant compounds is well advanced in the case of plastics (see Sec. XA), but in the case of fibers, effective approaches have not been documented. This may be due to several facts: chemical inertness does not easily allow for modifications involving covalent bonding; fiber properties are critically dependent on molecular weight, regularity, and molecular order; fiber production and applications have been limited. In a major use (carpeting), flame resistance has been attained through the use of flame-retardant compounds in the carpet backing (Nametz, 1970).

I. Specialty Fibers

Elastomeric fibers made from polyurethanes (Mark et al., 1968) and silk-like fibers, such as du Pont's "Qiana" polyamide, are new entries in the textile fiber field. To date, approaches to chemical modification of these fibers with flame-retardant compounds have not been reported.

Polyvinyl alcohol fibers have been developed in Japan (Mark et al., 1968), and were considered for commercialization in the U.S. in the early 1960s, but are not currently produced in the U.S. Modifications of polyvinyl alcohol

fibers to impart flame resistance have nevertheless been studied: conversion of hydroxyl groups to acetals using halogenated acetaldehyde or benzaldehydes, and esterification of hydroxyl groups with derivatives of phosphoric or phosphonic acids have been recorded in the technical literature.

J. Fiber Blends

Blends are textile materials made from yarns containing two or more different fibers. Blend fabrics have attained great commercial importance and have afforded opportunities for optimal utilization of fiber properties in textile products. Flammability and flame resistance of blends have received attention since 1968, and it was soon established that modification of these multicomponent substrates with flame retardants poses special problems (Tesoro and Meiser, 1970). The complexity of these problems is further increased by the large number of variables in the substrate (specific fibers, fiber content or percentage, melting vs. nonmelting behavior, etc.). Information recorded in the technical literature on the flammability behavior of blend fabrics has been reviewed (Tesoro, 1975), but it is not possible to propose generalizations regarding viable approaches to chemical modification of blends with flame retardants (Tesoro and Rivlin, 1971).

The most important blend fabrics are those made from polyester and cotton, generally (but not necessarily) containing 50% or 65% polyester. Modification of these fabrics with flame retardants can be approached by (1) blending modified (flame-resistant) polyester fiber with cotton; (2) finishing the

TABLE XX

Summary of Approaches to Modification of Polyester/Cotton Blends with Flame Retardants

Finishing System	Substrate-blends of cotton with	Reference
$(HOCH_2)_4P^+ X^-$ X = OH, Cℓ etc. (with coreactants)	Bromine-containing PET	Tesoro, 1973a.
$(HOCH_2)_4P^+ X^-$ with bromine-containing compounds	PET	Tesoro, 1973, Sello and Stevens, 1974, Reeves, 1974.
Phosphonium digomers	PET	Loss et al., 1973.
Decabromo diphenyl oxide + Sb_2O_3	PET	Mischutin, 1975b.
Methylphosphonic diamide	Bromine-containing PET and PET	Tesoro, 1976.

polyester/cotton blend fabric with flame retardants; (3) a combination of (1) and (2).

All these approaches have been explored, generally utilizing flame-retardant compounds which showed effectiveness on polyester (see Sec. IXD) and on cotton (see Sec. IXE). The use of modified polyester (bromine-containing PET copolymer, see Sec. IXD2 and Fig. 3) does not provide anadequate level of flame resistance since melt drip is inhibited by the presence of cotton. Modifications of the polyester specifically designed for approach (1) have not been reported, and research and development efforts have been directed primarily towards approaches (2) and (3)—namely, finishing. A summary of finishing approaches which have shown promise is presented in Table XX.

The problem of flame resistance in polyester/cotton blends has not been solved in practical terms. Ongoing efforts continue, and an extensive program supported by the National Bureau of Standards is in progress as part of the Experimental Technology Incentives Program (ETIP) (Barker, 1975).

X. PLASTICS

A. Thermoplastic Resins

Synthetic polymeric materials used extensively as structural components, electrical insulation, decorative parts, etc., include thermoplastic resins, and thermosetting resins. Those in the former class have also been designated as "engineering thermoplastics," or polymeric materials that can be melt processed into shaped articles for use in various applications over a wide range of temperatures, mechanical stresses, and chemical environments. Advantages of engineering thermoplastics over conventional materials such as wood, metals, or ceramics include such properties as low-cost fabrication, electrical properties, high strength/weight ratio, suitability for composites, corrosion resistance, etc. Flammability characteristics of thermoplastics vary (depending on the specific chemical structure) with respect to thermal degradation, ease of ignition, flame propagation, heat release, extinguishability, smoke generation, and evolution of toxic gases in burning. However, by definition, melting and dripping often occur before thermal degradation and burning on exposure to elevated temperature.

The physical response of thermoplastics plays an important role in the evaluation of their flammability behavior. This physical response (e.g., melting temperature, melt viscosity) is affected by the presence of additives such as flame-retardant compounds. Furthermore, as in the case of other polymeric materials, chemical modification with flame retardants can impair the very properties that make thermoplastics suitable for a particular application (see Sec. VI), and discussion of chemical modification of thermoplastics with flame retardants is, by necessity, only a general introductory survey of the state of the art, which does *not* attempt to cover specialized application technology or formulations.

1. Polyolefins

Polyolefins are extensively used as engineering thermoplastics in automotive, appliance, and electrical applications, and in carpet backings. In some of these applications (e.g., TV cabinets), flammability is of significant concern. At this time, the polymers of primary importance are polyethylene and polypropylene.

Polyolefins burn readily in air, with melting, dripping, and flowing of molten polymer. Essentially no soot and no residual char are formed. The thermal degradation products are primarily low molecular weight hydrocarbons which are very flammable. Little work has been done on the flame-retardant modification of polyolefins by incorporating comonomers in the polymer chain, or by graft copolymerization approaches, since modifications of this type would alter the properties of polyolefins drastically. Documented approaches deal primarily with the incorporation of "inert," polymer-insoluble additives (Kuryla and Papa, 1973). Research and development on these approaches has been aimed at attaining a sufficient level of flame

TABLE XXI

Halogenated Additives for Polyolefins[a]

Aliphatic chlorine-containing	Examples
	Polyepichlorohydrin
	Polyvinyl chloride
	Chlorinated paraffin
Aliphatic bromine-containing	
	Polyepibromohydrin
	Hexabromocyclododecane
	Tris(dibromopropyl) phosphate
Aromatic chlorine-containing	
	Pentachlorophenol
	Pentachloro diphenyl ether
Aromatic bromine-containing	
	Pentabromophenol
	Pentabromo diphenyl ether
	Decabromodiphenyl
	Tetrabromo bis-phenol A

[a]From Kuryla and Papa (1973) and Lyons (1970a).

resistance to "pass" a given test or standard, while maintaining adequate stability in melt-processing and performance properties in use.

In principle, effective flame-retardant additives in polyolefins would function by one or more of the following mechanisms: (1) promote char formation reducing the concentration of combustible fuel (by dehydrogenation, or by cross-linking);(2) modification of melt-flow characteristics, allowing enhanced dripping to carry away a significant part of the heat flux delivered to the polymer surface; (3) reduce the oxygen concentration in the flame and preignition zones of the burning polymer (flame quenching); (4) inhibit chain propagation reactions in the flame (flame poisoning). As a practical matter, halogen-containing compounds, halogen/antimony combinations and, to a lesser degree, phosphorus compounds, have significant applications.

Table XXI summarizes halogenated additives found to be of interest, either alone or in conjunction with antimony oxide as synergist. Direct halogenation (chlorination or bromination) has also been proposed for polypropylene.

TABLE XXII

Halogen-Containing Flame Retardants and Sb_2O_3 in Polypropylene

Flame retardant	Concentration %	Sb_2O_3 %	Oxygen Index (% O_2)
None	---	---	17.8
None	---	20	17.6-17.8[a]
Hexabromocyclo dodecane	4	---	20.2
	4	2	30.9
Pentaerythritol penta-	6	---	20.6
bromide	6	4	23.8
Polybeta-tribromoethyl	4	---	23.6
methacrylate	4	3	28.1
Chlorendic acid	10	---	19.7
	10	5	22.2
Tetraethylammonium	8	---	19.9
bromide	8	3.5	21.5

[a]Apparent oxygen index value may decrease due to inhibition of melt drip.

Generally, speaking, halogen-containing structures that are stable enough to survive processing temperatures (do not lose hydrogen halide) are required. Bromine is more effective than chlorine.

The synergism of antimony, generally introduced into the polymer as antimony trioxide (Sb_2O_3) with halogen-containing organic compounds for flame retardation in olefins is well documented. Recent work has been summarized (Pitts, 1972), concluding that the halogen compound and the antimony synergist react in the molten polymer to form volatile halides or oxyhalides of antimony, which subsequently decompose to the halides.

The effect of some typical halogen/antimony systems in polypropylene is illustrated by the oxygen index values summarized in Table XXII (Kuryla and Papa, 1973). It is interesting to note that the addition of Sb_2O_3 is not effective in the case of a salt (tetraethylammonium bromide) which does not release hydrogen halide.

Phosphorus compounds have been suggested as flame retardants for polyolefins (Lyons, 1970a). Triphenyl phosphate, phosphite, and phosphine have been shown to increase the oxygen index of polyethylene (Fenimore and Martin, 1966). It has been postulated that phosphoric acid is formed in the polymer melt and converted to polyphosphoric acid which then forms a coating or barrier on the polymer surface, separating the molten polymer from the flame front. Enhanced melt drip caused by phosphorus-containing additives may also be a factor. Synergistic and additive interactions of phosphorus and halogen have been observed for compounds containing both elements (e.g., halogenated phosphates) and for combinations of flame-retardant compounds.

In summary, then, the most effective flame retardants for polyolefins are those that can release halogen to the flame zone. Antimony synergism is explained by formation of volatile antimony halides. Decomposition of flame retardants to release halogenated fragments or hydrogen halide must allow the polyolefin to survive processing temperatures—either by selecting structures in which the onset of thermal degradation is programmed in an appropriate manner, or through the use of added stabilizers.

2. Styrene Polymers

Polystyrene (plastics or foams) and styrene copolymers (styrene-acrylonitrile copolymers-SAN and acrylonitrile-butadiene-styrene copolymers-ABS) have varied and important applications for automotive parts, furniture, insulation packaging, appliances, toys, etc. Performance properties and requirements for flame resistance vary over an enormous range, and problems of flame retardation accordingly vary in complexity, importance, and approach. As in the case of polyolefins, modification by incorporating comonomers or by grafting has not been studied in depth, but examples of flame-retardant comonomers have been reported and are included in the summary tables. The most widely used approach to reduced flammability has been through the use of flame-retardant additives.

Commercial flame retardants for polystyrene currently include chlorinated paraffins, chlorinated polyphenyls, tetrabromoethane, triaryl phosphates, and halogenated aliphatic phosphates. Flame-retardant compounds from other chemical classes have been tested, effective compounds generally containing phosphorus and/or halogen (Howarth et al., 1973). In addition, synergists and diluents (or fillers) play a significant role. Selected examples of flame-retardant compounds for polystyrene plastics are tabulated in Table XXIII with relevant references.

The same compounds have also been generally used as flame retardants for polystyrene foams, although in this case, the technology, flammability evaluation, and requirements are different, and specific details of formulation and processing are to be found in different publications or patents. Halogenation, halogenated styrene comonomers, halogen-containing additives (aliphatic, alicyclic, and aromatic), and phosphorus compounds are mentioned in the patent literature (Kuryla and Papa, 1973). Inorganic diluents and fillers are also claimed to be effective.

Many of the flame-retardant additives found effective for polystyrene (plastics and foams) are also claimed to be effective for styrene-acrylonitrile (SAN) and for acrylonitrile-butadiene-styrene (ABS) copolymers. Synergists of interest include antimony trioxide (in amounts depending on the type of halogen-containing flame retardant used), other antimony compounds, and other metal oxides. The synergism of peroxides with organic halogen compounds in polystyrene has received a great deal of attention since it was discovered (Eichorn, 1964). It was originally thought that peroxides would cause evolution of halogen-containing species to occur at a critically important stage of the polystyrene pyrolysis. However, this hypothesis has not been supported by experimental results, and the "apparent" synergism is more probably the result of an increased dripping tendency caused by accelerated polymer degradation in the presence of peroxides.

Reported synergism of nitrogen compounds which form free radicals, such as *N*-nitroso, *N*-chloro compounds, and azo compounds (Eichorn, 1964) with halogen may be similarly related to combined effects of the added compounds on the melt viscosity of the polymer.

3. Polyvinyl Chloride and Related Polymers

Unplasticized polyvinyl chloride (PVC) is inherently flame resistant due to its high chlorine content. This property has contributed greatly to the rapid growth of rigid PVC in construction, transportation, and electrical applications where flame resistance is an important consideration. However, most uses for PVC require compounding with plasticizers, heat stabilizers, and extenders in order to attain the desired properties. Compounding with these additives, particularly plasticizers, which are generally used in large amounts (40–100 parts per 100 parts of resin [phr]), significantly decreases chlorine content and increases the flammability of the product. Addition of flame retardants is required for plasticized PVC in uses where flame resistance is

TABLE XXIII

Examples of Flame Retardants for Polystyrene (PS) Plastics

Compound	Level	Remarks	Reference(s)
Halogen	0.8% Br	PS Halogenation	German Pat. 962,650 (1957), USP 3,104,214 (1963).
Monochlorostyrene	12-24% Cl	Comonomer	R. J. Dolinski et al., Ind. Eng. Chem. Prod. Res. Dev. 9, 292 (1970).
Dibromostyrene Vinyl bromide Bis-dibromopropyl fumarate	2-6% Br	Comonomer	P. Volans, Plastics Ind. Trans. J. Conf. Suppl., No. 2, 47 (1967).
Pentabromophenyl metacrylate	4.8% Br	Comonomer	Belgian Pat. 624,340 (1968).
Ammonium bromide	1-6%	Inorganic-additive	USP 3,132,045 (1964), USP 3,133,037 (1964), USP 3,108,016 (1964), German Pat. 1,269,800 (1968), German Pat. 1,251,946 (1967).
Tetrabromoethane[a]	1-5%	Additive with and without synergists	USP 3,061,584 (1962), USP 3,338,864 (1967), USP 3,284,544 (1966).
Chlorinated Wax[a]	7-35%	Additive with and without synergists	USP 2,582,452 (1952), USP 2,924,532 (1960), USP 2,669,521 (1954), USP 2,590,211 (1952).

Compound	Level	Remarks	Reference(s)
Hexahalo[b] cyclopentadiene	5%	(with Sb_2O_3)	French Pat. 1,523,752 (1968), Belgian Pat. 612,960 (1962).
Halogenated[b] cyclohexane	0.5-3%	---	British Pat.1,093,165 (1967), USP 3,004,935 (1961).
Hexabromo[b] cyclododecane	0.25-3%	---	French Pat. 1,537,753 (1968), German Pat. 1,222,670 (1966), British Pat. 895,609 (1962).
Tribromoaniline[c]	5-20%	(with Sb_2O_3)	German Pat. 1,103,020 (1961),
Bis dibromopropyl[c] phthalate	1.5-6%	---	USP 3,317,568 (1967), USP 3,236,659 (1966).
Tris dibromopropyl[d] phosphate	0.5-6%	---	USP 3,338,864 (1967), USP 3,397,216 (1968).
Tritolyl phosphate[d]	---	---	British Pat. 1,114,174 (1968).
Tris bromomethyl[d] phosphine oxide	---	---	USP 3,306,937 (1967).
Phosphine oxides[d]	15-30%	---	British Pat. 1,028,158 (1966).
Phosphonium halides[d]	0.5-25%	---	USP 3,333,005 (1967).

[a]Aliphatic halogen compounds.
[b]Alicyclic halogen compounds.
[c]Aromatic halogen compounds.
[d]Phosphorus compounds.

essential. The use of antimony oxide for synergistic interaction with the chlorine of the polymer is a common approach. Zinc borate has also been suggested as an effective adjunct to antimony oxide.

Fillers such as calcium carbonate, clay, or silica are often used as diluents, and aluminum trihydrate is a useful flame retardant, releasing water of hydration and cooling the flame. However, these inorganic additives affect the clarity and strength of the resin and, if clarity is essential, compatible liquid flame retardants must be used. Phosphate plasticizers, halogenated organic phosphate plasticizers, and chlorinated hydrocarbon extender plasticizers compounded with the PVC must be selected to meet exacting requirements: vapor pressure of the plasticizer, flexibility of the plasticized resin at low temperature, stability to processing temperatures, and resistance to aging must be considered. The effect of typical plasticizers on oxygen index is shown in Table XXIV (Kuryla and Papa, 1973), and it is clear that the effect on oxygen index is not a simple function of phosphorus content (Richardson and Snyder, 1970).

TABLE XXIV

Effect of Some Typical Plasticizers (80 phr) in PVC[a]

Plasticizer	% P in total compound	Oxygen Index
Dioctyl phthalate (DOP)	0	21.1
Trioctyl phosphate	3.18	24.6
Isodecyl diphenyl phosphate	3.54	25.1
DOP-Isodecyl diphenyl phosphate (1:1)	1.77	24.1
Tricresyl phosphate	3.76	29.8

[a]From Kuryla and Papa (1973).

Ultimately, the formulation of plasticized PVC requires an acceptable compromise of properties, compliance with flammability requirements, and cost. The choice is a pragmatic decision made by the technologist in industry. Information on compounding and uses of PVC (rigid and flexible), has been reviewed (Kuryla and Papa, 1973).

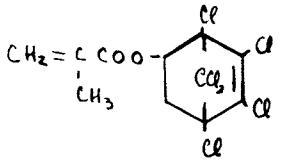
Latexes from polymers and copolymers of vinyl chloride, vinylidene chloride, and vinyl bromide have important applications (e.g., coatings, binders). Because of the high halogen content, these are often used without additional compounding in applications where flame resistance is important, although the addition of flame-retardant plasticizers may be required (Spencer, 1970), and addition of flame-retardant salts is recommended in some instances.

4. Acrylic Plastics

Acrylic plastics are generally polymers of methyl methacrylate, or copolymers of methyl methacrylate with other methacrylates, with acrylates, or with acrylonitrile. Acrylic plastics have excellent transparency, clarity, resistance to outdoor exposure, and dimensional stability. They are used in many applications (including aircraft windows, light fixtures, automobile lenses, electrical insulators) where these properties are critical. The necessity to maintain properties such as clarity and resistance to weathering imposes considerable restrictions on the approaches which can be used in flame retardation of acrylic plastics. The flammability behavior of acrylic plastics in conventional laboratory tests has been rated as roughly comparable to that of wood, but

TABLE XXV

Examples of Flame Retardants for Acrylic Plastics (polymethyl methacrylate)

Compound	Reference(s)
Comonomers:	
$CH_2 = C(CH_3)COOC_2H_4Br$	USP 3,219,640 (1965), German Pat. 1,300,295 (1969).
	German Pat. 1,066,743 (1959).
$CH_2 = C(CH_3)-COO\ C_2H_4P(O)(OC_2H_5)_2$	USP 2,934,554 (1960), USP 2,993,033 (1961), A. N. Pudovek, Vysokomolekul .Soedin 5 (9) 1376 (1963).
Additives	
Halogenated phosphates) Halogenated polyphosphonates)	R.A. Cass and L.O. Raether, ACS - Div. Org. Coatings and Plastics Preprints 23 (1) 82 (1963), Mod.Plastics 41, 167 (1963).
Chlorinated hydrocarbons) with antimony compounds)	Belgian Pat. 614,296 (1962), USP 2,664,411 (1953), French Pat. 1,157,208 (1958).

this approximation may be grossly misleading in some instances because of the differences in physical response. Generalizations concerning the flammability of acrylic plastics should be avoided.

Approaches to flame retardation of acrylic plastics differ from those used for acrylic fibers (see Sec. IXF): in the case of fibers (polyacrylonitrile), halogen-containing comonomers are used almost exclusively, while in the case of acrylic plastics, the use of additives is also important. On exposure to high temperature, polymethyl methacrylate depolymerizes with the formation of monomer (Conley, 1970). Flame retardants that have been used to inhibit depolymerization and burning include comonomers and additives, and halogen and phosphorus compounds. Examples of each type are summarized in Table XXV. In general, the copolymer approach has considerable effect on the properties of the acrylic composition because the amount of flame-retardant comonomer required to decrease flammability is high (about 10–20%). It has been suggested (Cass and Raether, 1963) that halogenated polyphosphonates are efficient flame retardants for polymethyl methacrylate, and that higher molecular weight additives are less detrimental to polymer properties than low molecular weight compounds of comparable structure. It is postulated that the flame-retardant additive should be compatible with the substrate polymer without appreciable plasticizing effect on it. Generally speaking, combinations of phosphorus and halogen are reported to be most effective (Grundfest and Young, 1961; Miles, 1968) at levels of about 1–3% P in combination with 2–10% halogen. Flame-resistant acrylic plastics are not currently in widespread commercial use.

5. Nylons

Nylon plastics are made primarily from nylon 6,6 (poly-hexamethylene adipamide) or from nylon 6 (polycaprolactam). At this time, their major application is for small automotive parts, and in a variety of extrusion and molding applications in which fire safety problems have not been considered important. However, the use of nylon plastics for other applications is foreseen and flammability behavior of nylon plastics may become of interest.

Nylon moldings are often described as self-extinguishing due to the tendency of the polymer to drip away from the flame: if dripping is prevented, nylon sustains combustion and burns with a smoky flame. Fire retardants for nylon plastics are reportedly based on phosphorus- and/or halogen-containing additives with or without the addition of antimony or other metal oxides as synergists (Lewin et al., 1975). The addition of drip promoters such as thiourea or ammonium thiocyanate has also been proposed (Douglas, 1957) (see also Sec. IXE). Many nylon molding and extrusion compositions contain glass fibers or particulate mineral fillers (as much as 50% by weight). In these filled materials, where dripping is inhibited, the plastic tends to burn more readily than its unfilled counterpart, and the need for flame-retardant additives may be greater.

6. *Linear Polyesters*

Polyethylene terephthalate and polytetramethylene terephthalate have been investigated for injection molding applications, and the latter is used in small automotive parts and in electrical applications (Borman and Kramer, 1974). Many compositions are reinforced with glass fibers or fillers. Flame retardation is approached by incorporating halogen-containing materials as comonomers or additives (Shalaby and Pearce, 1974) (see also Sec. IXD). Metal/oxide synergists are frequently included.

7. *Cellulosics*

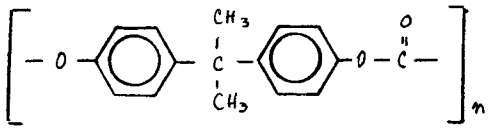
Cellulose derivatives that are useful as plastics include esters (organic and inorganic) and ethers, as well as regenerated cellulose which is used in films (cellophane). In fact, celluloid, the first synthetic plastic, commercialized in 1870, consisted of cellulose nitrate plasticized with camphor. Cellulose nitrate is currently used only in coatings: it ignites readily, burns vigorously, and may be replaced by less flammable materials in the future. Organic esters (acetate, propionate, butyrate) of cellulose are tough, clear plastics with good electrical properties used in films and sheets, in injection molding, and in extrusion. Halogen- and phosphorus-containing plasticizers have been used to decrease flammability (Howarth et al., 1973). Cellulose ethers (e.g., ethyl cellulose) are used in specialized applications (e.g., small appliance parts) and are not generally modified with flame retardants.

8. *Polyacetals*

Commercial polyacetals are formaldehyde polymers and copolymers terminated (capped) with ester or other groups for stabilization. They are used in automotive parts, appliances, and plumbing fixtures. Their unique alternating carbon-oxygen backbone structure governs their thermal degradation behavior: the polymer pyrolyzes at relatively low temperature (~230°C), yielding formaldehyde which burns without smoke at low oxygen concentration. The nature of these pyrolytic reactions is such that it has been essentially impossible to modify the flammability of polyacetals.

9. *Polycarbonates*

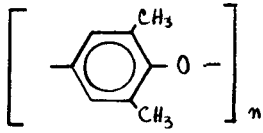
Polycarbonates are a special class of polyesters derived from bis phenols and phosgene:



Commercial products are based on bis phenol A, and some contain fibrous or particulate fillers. Unmodified polycarbonates are significantly less flammable than polyolefins, styrene polymers, or acrylics. This is indicated by their relatively high oxygen index (24.9). Their fire resistance can be further improved by using halogenated bis-phenols as comonomers in monomer synthesis, or by the use of halogen-containing additives, with or without antimony oxide (Howarth et al., 1973).

10. Polyaryl Ethers

A recently developed, commercially available polyaryl ether based on the oxidative coupling of 2,6 xylenol



is a tough, chemically resistant thermoplastic with good thermal stability which has been proposed for several engineering applications. It is also used in blends with polystyrenes (trade named Noryl), which have properties (and cost) intermediate between those of ABS resins and polycarbonates. The flammability of polyaryl ethers is low as the polymers tend to char. In blends with polystyrene (Noryl) the presence of the polyaryl ether reduces the flammability of the polystyrene; fire-retardant additives or coreactants are also used in Noryl resins to decrease flammability further.

B. Thermosetting Resins

1. Phenolic Resins

Phenolic resins are condensation products of phenols with aldehydes (almost exclusively formaldehyde) classified as Novolaks, or Resoles depending on whether or not they contain reactive methylol (CH_2OH) groups. Phenolics are widely used as molding resins for automotive, radio, television, and electrical and appliance parts. They are also used as laminating resins and as adhesives. Phenolic resins do not ignite easily on exposure to a flame source, and are considered to be inherently flame resistant. However, on prolonged exposure to heat, phenolics (particularly foams) can smolder and char until consumed. This phenomenon, called "punking," can be inhibited by specific substances: boric acid (Quarles and Baumann, 1967), aluminum chloride (Erickson, 1967), antimony oxide, organic amides, and others are claimed in the patent literature (Kuryla and Papa, 1973).

Improved flame resistance in phenolic resins has been claimed through the

use of phosphorus compounds, either as additives, or reacted with phenolic hydroxyl groups. It has been suggested that self-extinguishing properties are obtained when 6% phosphorus, or 2% phosphorus + 2% nitrogen are present in the resin (Lyons, 1970a). The patent literature includes claims for the flame-retardant effectiveness of boric acid, and of halogen compounds in phenolics (Kuryla and Papa, 1973). Flame retardants offered commercially for use in phenolic resins are generally phosphate or halogenated phosphate compounds used as additives (and not as reactants).

2. Amino Resins (Urea-Formaldehyde and Melamine-Formaldehyde Resins)

Condensation products of formaldehyde with urea and with melamine, commonly called amino resins, are important in molding/applications, in adhesives, decorative laminates, and in other uses, such as textile finishing. Amino resins are inherently flame resistant and generate little smoke in burning. Little work has been done on flame retardation in these polymers. Phosphorus-containing additives (including phosphonic acid salts and more complex organic phosphorus compounds) have been claimed in the patent literature as effective flame retardants for amino resins (Kuryla and Papa, 1973). More importantly, amino resins have been used in conjunction with phosphorus-containing flame-retardant systems in cellulose (wood and cotton fibers) where they have provided a source of nitrogen in the flame-retardant system. The synergistic interaction of phosphorus and nitrogen in flame retardation of cellulosic polymers is frequently attained by incorporating melamine-formaldehyde condensation products (see Sec. IXA), which thus become a part of the flame-retardant system (Lyons, 1970a).

3. Unsaturated Polyester Resins (and Alkyds)

Two classes of thermosetting polyester resins are important: the so-called unsaturated polyesters are prepared by condensing a glycol with dibasic acids (saturated and unsaturated), adding styrene (or other vinyl monomer), and cross-linking through additional copolymerization of the added monomer with the chain unsaturation.

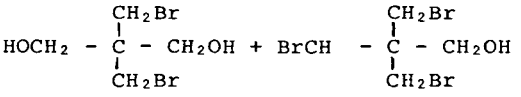
The alkyd resins are prepared by polycondensation of a dibasic acid (typically phthalic acid) and glycol (typically ethylene glycol) in the presence of polyunsaturated fatty acids from vegetable oils (linseed, soybean, and tung oil). Cross-linking is accomplished by oxidation of the unsaturated pendant chains, usually accelerated by driers such as metal naphthenates, lead soaps, etc. Alkyd resins are used almost exclusively as surface coatings and their flammability properties are modified on the basis of principles of coating technology (Sec. XIII).

Unsaturated polyesters, on the other hand, are important polymeric materials in the construction industry, the chemical process industry, the manufacture of small boats, etc. They are generally used as glass-fiber-reinforced or filled composites, and for this reason much of the information available in

the literature on the flammability behavior of the polyester resins concerns the filled or glass-reinforced materials. Unsaturated polyester resins modified with flame retardants are currently a small fraction of the large total volume used. However, this fraction is expected to increase rapidly as awareness and concern for flammability and fire safety in materials increase (Stepniczka, 1976).

Fire resistance of unsaturated polyesters can be improved by (1) addition of inorganic fillers, (2) addition of organic fire retardants, (3) modification of the monomers (acid, alcohol, or unsaturated monomer), (4) complexing of organometallic compounds with the resin (Nametz, 1967; Roberts et al., 1964).

Among fire-retardant fillers, the most widely used and effective is hydrated alumina. Phosphorus esters and chlorinated waxes have been proposed as organic flame-retardant additives. Bis-chlorendo-cyclooctane is reported to be particularly efficient (Pattison and Hindersinn, 1971). Halogen-containing diols, e.g., amixture of dibromo neopentyl glycol and tribromomethyl carbitol (see below)



of halogen-containing unsaturated acids (e.g., chloromaleic acid) have been suggested, but the most successful approach has been the use of halogenated saturated acids (tetrabromophthalic anhydride, tetrachlorophthalic anhydride, chlorendic acid, or anhydride are examples) (Stepniczka, 1976). Antimony oxide is sometimes used in conjunction with the halogenated monomers.

Lyons (1970a) presents a comprehensive summary of compounds proposed as flame retardants in unsaturated polyester resins, and summarizes the chemical requirements for flame resistance as follows (approximate):

5%	P
1%	P + 15–20% Cl
2%	P + 6% Br
25%	Cl
12–15%	Br
2%	Sb_4O_6 + 16–18% Cl (or 8.9% Br)

Estimates of requirements based on current test methodology, including oxygen index, remain consistent with the ranges indicated. Oxygen index values of 35–40 have been reported at high halogen contents for resins prepared from halogenated intermediates (Stepniczka, 1976) and the effect of structure of the halogenated compound (comonomer) on its flame-retardant effectiveness in the resin has been found to be small (Honig, 1976).

4. *Epoxy Resins*

Epoxy resins are specialty thermosetting resins obtained from reaction of a polyfunctional epoxy prepolymer (which, in turn, is generally prepared from a polyfunctional phenolic compound and epichlorohydrin) with cross-linking agents (generally called "hardeners") which may be basic (e.g., amines) or acidic (e.g., anhydrides). The flammability of epoxy resins can be modified by the addition of flame retardants such as halogenated phosphates, by the incorporation of relatively large amounts (up to 50% on the weight of resin) of hydrated alumina, or by replacing part of the phenolic precursor with a halogenated phenol (e.g., tetrabromobis-phenol A). A large number of fire-retardant compounds have been claimed (Lyons, 1970), but few are used in commerce. The effects of flame-retardant compounds on the oxygen index of several epoxy resins are discussed in a publication (Martin and Price, 1968) which also summarizes the major relevant concepts and structures.

5. *Polyurethanes*

Major approaches to the chemical modification of polyurethanes with flame-retardant compounds are discussed in Sec. XIA1 in conjunction with flame retardation of polyurethane foams. In the case of polyurethane compositions which are not used for rigid or flexible foams, but as solid plastics (e.g., molding resins), reduced flammability is somewhat easier to attain the effect of added flame retardants on polymer properties may be less critical, and the burning behavior of the solid may be more easily altered than in the case of the foams, where low density and high availability of oxygen to burning surfaces increase the severity of the flammability problems. Thermal degradation mechanisms and the chemistry of the approaches are not substantially different in the case of polyurethane solid and cellular plastics; flammability evaluation, criteria for acceptance, and commercial viability, on the other hand, differ considerably in the two situations. Polyols or polyisocyanates containing phosphorus and/or halogen are used as comonomers in the preparation of flame-resistant polyurethane plastics (Lyons, 1970a,b; Frisch, 1965; Dickert and Toone, 1965).

The characteristics of solid and cellular polyurethane plastics, of polyurethane coatings, and polyurethane elastomers can be appreciated by reviewing works on polyurethane technology (Frisch and Saunders, 1972, 1973; Backus, 1974). Generalizations concerning the amounts of flame retardants required to attain self-extinguishing behavior in polyurethanes (not identified as to specific composition, chemical structure, or type) have been estimated (Lyons, 1970a; Lewin et al., 1975) in the context of various compositions and flammability tests and may be summarized as follows: % P: 1–2, % Cl: 10–25, % Br: 5–15. Chlorine and bromine are reportedly more effective in conjunction with phosphorus *or* with antimony oxide, and specific combinations of these elements are selected on the basis of their effects on other properties and cost.

XI. FOAMS (CELLULAR PLASTICS)

Foams are an important class of polymeric materials: they pose special problems with regard to flammability behavior, and with regard to the possibility of modifying them to impart flame resistance. Excluding naturally occurring foamed polymers (pumice, meerschaum, sponge, cork), foams are generally made from complex multicomponent systems. They may be flexible or rigid, blown or syntactic, open cell or closed cell, etc. Foams may have a modified surface or skin, and may contain fibers or fillers. The technology and classification of foams is clearly beyond the scope of this discussion. The importance of foams in cushioning applications (flexible) and in thermal insulation (rigid) cannot, however, be overemphasized, and emerging concerns about fire safety in the environment have greatly increased the level of technical effort on modification of foams with flame retardants.

Independently of chemical composition in foams, the high surface area per unit mass leads to increased flammability. [The density of foams is of the order of 2 lb/ft^3 (0.032 g/cm^3) as compared to about 55–75 lb/ft^3 (0.9–1.2 g/cm^3) for plastics.]

There are several reasons for this: the large surface exposed increases availability of oxygen and, thus, rate of pyrolysis; because of high gas content in the foam, the specific heat per unit volume is low; because of low thermal conductivity, heat is accumulated on the surface rather than dissipated to the underlying material, thus enhancing pyrolysis and flame propagation at the surface. Other factors may moderate these effects; for example, the total heat available is low (low amount of fuel per unit volume); melting of the foam ahead of the flame in some cases may cause the material to recede and the flame to extinguish.

In addition to these considerations of geometry and structure, the chemical composition of the foam is an essential factor in its flammability behavior, and in the approaches to chemical modification that are both viable and effective. Polyurethane foams (both rigid and flexible) and polystyrene rigid foams comprise the largest share of the foam market.

A. Rigid Foams

Like plastics in general, rigid foams may be thermoplastic or thermosetting. The former can be made from polystyrene, ABS, polyethylene, polycarbonate, polyvinyl chloride, etc. Thermoplastic foams melt and generally depolymerize when heated. Thermosetting foams can be made from phenolic resins, cross-linked polyurethanes, etc. Rigid foams which are not made from inherently flame-resistant polymers (e.g., polyimide) may be fire-retarded by several approaches, including the use of flame-retardant comonomers or additives in the polymer of formulation, the application of fire-retardant coatings to the foamed surface, and the introduction of inert fillers to control flame spread.

1. Polyurethane Foams

The flammability of rigid (cross-linked) polyurethane foams depends in part on the cross-link density, and on the thermal stability of specific groups in the polymer network. Thus, it is possible to prepare foams which exhibit adequate fire resistance for some applications by using highly branched polyols (e.g., sucrose), or polymeric isocyanates, or catalysts which induce trimerization of isocyanate to thermally stable isocyanurate rings. These approaches increase cross-link density, minimize the concentration of thermally labile urethane groups in the cross-linked polymer, and enhance the tendency to char formation on exposure to elevated temperature (Frisch and Saunders, 1973). Other performance properties of the foam are, however, altered, and the control of flammability through this synthetic approach has found limited and specialized application to date. The effect of polyurethane structure on flammability has been studied in model polymers (Backus et al., 1968).

More generally, fire resistance is attained in rigid polyurethane foams by incorporation of phosphorus and/or halogen compounds in the polymer (reactive flame retardants), or in the formulation (additive flame retardants). Compounds and approaches documented in the technical literature are covered in several comprehensive reviews (Papa, 1970, 1972; Kuryla and Papa, 1975), and the number of specific patent disclosures and technical publications is in the hundreds at least. The role of phosphorus, chlorine, and bromine in decreasing flammability of rigid polyurethane foams has been systematically investigated (Piechota, 1965), and the conclusion was reached that the optimum relationship of phosphorus to bromine for maximum fire resistance in rigid foams corresponds to the empirical equation

$$\%\,P + \%Br/10 = 1.5$$

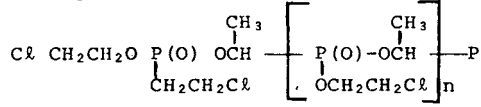
This predictive generalization was reached on the basis of flammability tests (e.g., ASTM D-1692), which are currently in question as to validity. It remains to be established whether similar conclusions would be reached by employing more meaningful tests such as oxygen index.

Furthermore, the effectiveness of a given flame-retardant compound or system varies with the particular foam formulation or structure as indicated above. Discussion of effective flame retardants provides only a preliminary indication of approaches, to be examined and interpreted only with reference to specific foam formulations and specific test methods for flammability evaluation.

Additive flame retardants are more important for flexible polyurethane foams (see Sec. XIB1), while reactive flame retardants (generally phosphorus and/or halogen containing polyols) are more important for rigid foams. The reasons for this preference are not clear, but they appear to be related to foam processability, properties, and technological requirements rather than to the specific efficiency of the compounds as flame retardants. Thus, the selection

TABLE XXVI

Examples of Additive Flame Retardants for Polyurethane Foams

	Flame retardant system	Reference
1.	Antimony oxide - Halogen compound	
	- polyvinylidene chloride	C. J. Hilado et al., J.Cell Plastics 6(5) 215 (1970).
	- trichloro, tribromo phenol	Z.E. Idles, Trans. J. Plastics Inst. Conf. Suppl. 2, 33 (1967).
	- polyvinyl chloride + ZnO	USP 3,574,149 (1971).
2.	Alumina trihydrate + halogenated phosphate	USP 3,262,894 (1966).
3.	Phosphates e.g. tris chloroethyl phosphate	C. J. Hilado et al., J. Cell Plastics 4, 1 (1968).
	tris(2,3 dibromo-propyl) phosphate	R. M. Pruit, J. Cell Plastics 6(6) 262 (1970).
4.	Phosphonates e.g. $CH_3CH_2[P(O)(OC_2H_5)_2]_2$	USP 3,664,975 (1972).
	Aminomethyl phosphonates	West German Pat. 2,224,163 (1971).
5.	Phosphites e.g. cyclic phosphites	USP 3,412,051 (1968)
6.	Halogenated Polyphosphonates e.g. Phosgard C-22R	Monsanto Chemical Co. Data Sheet 10635-1.
		
7.	Brominated aromatics e.g. hexa-bromobiphenyl, hexabromobenzene	Michigan Chemical Corp. Tech data FIREMASTER HBB, FF-1, FF-2 (1971).

of flame retardants for polyurethane foams changes as requirements and technology are modified. The use of flame retardants is more significant for rigid foams than for flexible foams, probably because chemical modification can be attained more easily without impairing critical performance properties in the former case. Tables XXVI and XXVII summarize some examples of flame retardants found effective in polyurethane foams. These may be used commercially and are, in any event, of more than passing interest. The use of additives (Table XXVI) requires skillful manipulation of the foam formulation to allow for incorporating amounts of flame retardants that may be as high as 20%. The use of reactives (Table XXVII) necessitates the synthesis and characterization of polymers and foams in which part, or all, of a given starting material (generally the polyol) is replaced by phosphorus-containing and/or halogen-containing monomers.

Although the flame-retardant content needed cannot be defined without

TABLE XXVII

Examples of Reactive Flame Retardants for Polyurethane Foams[a]

Type	Example(s)	Reference(s)
Phosphate Polyols	Reaction products of phosphoric acid and propylene oxide	USP 3,369,060(1968), USP 3,402,132(1968), USP 3,499,009(1970), USP 3,699,060(1972), USP 3,525,705(1970).
		J.J. Anderson, Ind.Eng.Chem.Prod. Res. Dev. 2, 260 (1963).
Phosphonate Polyols	Dialkanolaminomethyl phosphonates	USP 3,707,587(1972), USP 3,555,124(1971), USP 3,235,517(1966), USP 3,076,010(1963).
	Bis-(aminomethyl phosphonate)diols	Canadian Pat. 875,563 (1971).
		F.H. Otey, et al., J.Cell Plastics, 3(3), 138 (1967).
	Alkylene oxide adducts of phosphonic acids	USP 3,474,047(1969), USP 3,458,457(1969), USP 3,318,855(1967).
Misc. Phosphorus-containing diols	Phosphoramidates	USP 3,584,085(1971), USP 3,597,503(1971).
	Methyl Phosphine oxides	USP 3,732,316(1973).
Phosphorus and halogen-containing polyols	Reaction products of chlorendic acid with phosphites and glycols/polyols/ epoxides	USP 3,214,396(1965), USP 3,214,395(1965), USP 3,214,394(1965), USP 3,249,562(1965).
	Condensation products of tetrabromophthalic anhydride and phosphorus-containing polyols	USP 3,565,812(1971), USP 3,419,642(1968), USP 3,639,542(1972), USP 3,585,185(1971).
Halogen-containing hydroxyl compounds	Polyepichlorohydrin	Canadian Pat. 855,274 (1970).
	Dibromoneopentyl glycol	USP 3,692,707(1972).
	Brominated castor oil	USP 3,704,256(1972).
	Dibromopropyl ethers of polyols	USP 3,474,148(1969), USP 3,567,665(1971).
	Condensation products of polyols + halogenated acids	USP 3,642,646(1972).
	Halogenated phenols	British Pat. 1,079,984 (1967).

[a]Source: Kuryla and Papa (1974), Vol. 3, pp. 76–79.

reference to the specific foam formulation and test method, the amounts of flame-retarding elements required to impart a given level of flame resistance have been discussed in the literature. In addition to the generalizations cited above (Piechota, 1965), it has been suggested (Dickert and Toone, 1965) that ranges of flame retardants used to give a "nonburning" rigid foam in ASTM test D-1692-59T should be equivalent to 6.5–13% Cl, 5.0–10% Br, 1.0–2.0% P. The relative effectiveness of phosphorus compounds and of halogen compounds have also been compared (Lyons, 1970a).

New concerns have emerged over smoke evolution from fire-retarded polyurethane foams and, perhaps more importantly, over the toxicity of thermal degradation and combustion products. Significant amounts of hydrogen cyanide have been detected in combustion products of unmodified polyurethanes (Sumi and Tsuchiya, 1973). The isolation of a highly toxic cyclic phosphate ester has been reported from combustion products of foams in which both a trimethylol propane polyol and an aminophosphonate flame retardant are used (Petajan et al., 1975). A great deal of research work is currently in progress on smoke and toxic gas evolution from fire-resistant rigid foams, and on improved methodology for testing and evaluation of these.

2. Polystyrene Foams

The major use of polystyrene foams is currently in packaging, with additional and growing usage in construction and appliances. Flammability characteristics of polystyrene foams are essentially as discussed for polystyrene plastics (Section XA2), with added considerations derived from the low density (foam structure). Fire-retarded polystyrene foams (reportedly available for use in construction) contain acetylene tetrabromide and copper phthalocyanine (Frisch and Saunders, 1973). Another approach proposed is the addition of small amounts of additives that promote thermal degradation, melting, and dripping (Gouninlock et al., 1971), but the utility of this concept clearly depends on whether the position of the foam part allows the polymer to drip away without continuing to burn.

The applications of polystyrene foams to date have been such that limited work has been carried out on modification with flame retardants, but activity in this area will probably increase.

3. Other Rigid Foams

Among applications of polyolefin foams are packaging, weatherstripping, safety padding, and telecommunication cable insulation. Flammability performance of polyolefin foams is similar to that of the solid plastic (see Sec. XG1). Where flame resistance is required as, for example, in flotation devices used in aircraft seat cushions, either antimony oxide/aliphatic chlorine compound combinations (Howarth et al., 1973) or phosphorus-containing additives are used.

Rigid polyvinyl chloride foams find some use in construction and in aircraft, and are inherently fire resistant—not chemically modified with flame retardants (see Sec. XA3).

Phenolic foams have good thermal stability and a high tendency to char formation, but smoldering and "punking" can consume the foam (see Sec. XB1) after removal of the ingition source. Punking can be prevented by the addition of boric acid/oxalic acid and ferric/aluminum chloride as the foaming catalysts (Quarles and Baumann, 1967).

B. Flexible Foams

Flexible foams can be made from practically any elastomer and they have great importance in many applications (mattresses, cushioning, rug underlay). Foam rubber made in dry compounding with chemical blowing agents (generally referred to as sponge rubber) and latex foam rubber are made from natural rubber or from styrene-butadiene rubber mainly. Polychloroprene (neoprene) latex foam is inherently fire resistant, due to the high chlorine content, and can be further fire-retarded by posttreatment with ammonium sulfamate, or with melamine-aldehyde condensation products (Carl, 1963).

Fire retardation of hydrocarbon sponge foam and latex foams has been reviewed (Hecker, 1968; Kuryla and Papa, 1973), but the technology is not advanced.

Flexible polyurethane foams currently account for over two-thirds of all flexible foams. Approaches to fire retardation in flexible polyurethane foams are similar to those used for rigid polyurethane foams (see Sec.XIA1). However, in the case of flexible polyurethane foams, it is extremely difficult to attain adequate fire resistance without loss of properties, and much work remains to be done.

Flexible foams have also been made from thermally stable polymers (polyimides, phosphazenes) and these are being evaluated in uses where a high level of fire resistance is critical (e.g., aircraft seat cushions).

XII. ELASTOMERS

Elastomers are distinguished from other polymeric materials by their ability to sustain large (up to 1000%) reversible deformation. This critical property of elastomers (rubbers) is attained in linear flexible polymers cross-linked to form a three-dimensional network, and in heterogeneous (generally two-phase) systems in which glassy or crystalline domains interspersed with a rubbery matrix act as the junction points of a cross-linked network. Elastomers of major commercial importance are natural rubber, styrene-butadiene, polybutadiene, polychloroprene, and polyisoprene.

Table XXVIII summarizes polymer structures present in elastomers. It is thought useful to present such a summary here, since flammability and ap-

TABLE XXVIII

Elastomer Structures

Elastomer type	Repeating unit	Reference(s)
Natural rubber (cis-1,4 polyisoprene)	$[-CH_2-C(H)=C(CH_3)-CH_2-]$	Morton, 1973, Winspear, 1972.
Styrene-butadiene rubber	Random copolymer $C_6H_5CH = CH_2$ $+ CH_2 = CH - CH = CH_2$	Morton, 1973, Winspear, 1972.
Butyl rubber	$[-CH_2 - C(CH_3)_2-]$	Morton, 1973, Winspear, 1972.
Ethylene-Propylene rubber	Random copolymer $CH_2 = CH_2$ + $CH_2 = CH(CH_3)$	Morton, 1973, Winspear, 1972.
Polychloroprene (neoprene)	$[-CH_2-C(H)=C(Cl)-CH_2-]$	Murray and Thompson, 1963.
Rubber hydrochloride	$[-CH_2 - C(Cl)(CH_3) - CH_2CH_2-]$	
Chlorinated and chlorosulfonated polyolefins	---	Winslow et al., 1971.
Polyepichlorohydrin	$[-O-CH_2 - CH(CH_2Cl)-]$	Willis et al., 1965.
Nitrile rubbers	$[-CH_2-CH(CN)-]$	Hofman, 1963.
Polyacrylate elastomers	Copolymers, e.g.: $CH_2 = CH(COOC_2H_5)$ $= +CH_2+ CH(OCH_2CH_2Cl)$	Morton, 1973.
Polyurethane elastomers	$[-O\ CONH\ R\ NH\ COOR'-]$	Saunders and Frisch, 1962, Backus, 1974.
Polysulfide rubbers (Thiokols)		Morton, 1973.
Fluorocarbon elastomers	Copolymers, e.g. $CF_2 = CF(CF_3)$ $+CH_2 = CF_2$	Arnold, 1973.
Silicone rubbers	$[-Si(R)_2 - O-]$	Laur and Guy, 1970.
Phosphonitrilic elastomers	$[-P(OR)_2 = N-]$	Hagnauer and Schneider, 1972.

proaches to flame retardation can be indicated with reference to the type of polymer involved. Approaches to fire retardation in elastomers have been reviewed in recent books (Kuryla and Papa, 1973; Lewin et al., 1975).

Natural rubber (essentially *cis*-1,4 polyisoprene) and synthetic hydrocarbon elastomers (polyisoprene, polybutadiene, styrene-butadiene rubber, polyisobutylene or butyl rubber, and ethylene-propylene rubber), which are used in large volume, all burn readily with much smoke in the absence of fire retardants. Since these rubbers are generally formulated with fillers, the use of aluminum trihydrate as filler offers a significant opportunity to reduce flammability and smoke evolution (Hecker, 1968; Dalzell and Nulph, 1970). The effect of fillers on flammability has been investigated extensively (Trexler, 1973; Hecker et al., 1973). Other approaches to fire retardation include halogenation and incorporation of chlorinated paraffins or other halogenated additives (Lewin et al., 1975).

Phosphorus compounds such a tributyl phosphate and triphenyl phosphate have been suggested, and are reported to be less objectionable than halogen compounds in terms of their effect on the aging properties of the elastomer (Lewin et al., 1975).

For synthetic hydrocarbon rubbers, polymer structure modification through the introduction of aromatic segments to decrease flammability has not been considered, since increased rigidity of the molecule would inevitably result in impairment of elastomeric properties.

Halogenated elastomers (e.g., polychloroprene) are less flammable than hydrocarbon elastomers, although evolution of smoke and hydrogen halide on exposure to elevated temperature pose other problems in terms of fire safety. Flammability characteristics of polychloroprene have been discussed (McCormack, 1972), and the effect of additives and fillers on oxygen index has been investigated in detail (Johnson, 1974).

Optimum fire resistance in elastomers can be attained through the synthesis of specialty elastomers, which are inherently nonflammable because part or all of the carbon in the polymer backbone is replaced by inorganic elements: silicone elastomers (Laur and Guy, 1970) and phosphonitrilic elastomers (Hagnauer and Schneider, 1972) are example of such advanced (developmental) elastomeric materials.

XIII. COATINGS

The use of fire-retardant coatings is one of the oldest methods for protecting flammable substrates. By definition, this approach does not entail chemical modification of the substrate, but rather the addition of a protective layer which alters the heat flux to the substrate and can (to varying degrees) inhibit its thermal degradation, ignition, or combustion.

Fire-retardant coatings may be nonintumescent or intumescent; the former are older, more widely used (e.g., marine paint), and more economical, while the latter provide a greater degree of protection to the underlying substrate.

A. Nonintumescent Coatings

Nonintumescent fire-retardant coatings are most frequently based on halogenated alkyd resins (see Sec. XB3): chlorinated diacids or anhydrides such as chlorendic anhydride or tetrachlorophthalic anhydride are used as monomers in the alkyd resin formulation (Cleaver, 1973) with appropriate modifications in processing conditions so as to avoid side effects (e.g., discoloration). This approach (chlorinated alkyd coatings) provides good performance and some fire resistance at low cost. Another approach involves the use of fire-retardant additives (rather than coreactants) in the alkyd coating formulation (Lyons, 1970a; Bhatnagar, 1972): specialized knowledge of the technology is essential for the selection of the additives, since these must be compatible with the paint vehicle as well as with the resin—and must not impair the properties of the coating. Chlorinated paraffins with antimony oxide as synergist are reportedly effective (Touval, 1972), and partial replacement of the antimony oxide with stannic oxide and zinc borate has been proposed (Bower et al., 1972).

The use of fillers such as aluminum hydrate is limited to opaque low-gloss coatings, since the high filler loadings needed affect clarity and gloss in a significant way.

Resins other than alkyds (polyurethanes, epoxys) are used to a much smaller extent in coatings. Heat-cured coatings based on melamine/formaldehyde or phenol/formaldehyde have significant utility in facotyr-coated wood paneling. Modification of these resins with fire retardants is not generally considered necessary (see Sec. XB).

B. Intumescent Coatings

The phenomenon of intumescence ("enlarging, swelling, or bubbling up—as under the action of heat," Webster) can be simply demonstrated by reacting sugar with sulfuric acid: the sugar is dehydrated exothermically, the water formed evaporates, leaving a carbonaceous char which is expanded into foam by the escaping water vapor. The effectiveness of intumescent coatings is thus based on the formation of foamed carbonaceous char which protects the underlying substrate from incident heat. Intumescent coatings have been reviewed (Vandersall, 1971) and a detailed discussion of their chemistry is beyond the scope of this review. However, since the concept of intumescence provides an important approach to fire retardation in polymeric substrates, the major factors involved will be outlined below.

Intumescent coatings contain several key components which are necessary to bring about the formation of the protective char:

A *catalyst* (which triggers the first of several reactions when the coating film is heated); a *carbonific compound* (which produces the carbonaceous residue); a *spumific compound* (which decomposes producing large quantities of gas); and a *resin binder* (which forms a skin over the foam and prevents it from collapsing). In addition to these key components, other ingredients used

in conventional coatings (pigments, driers, leveling agents, thinners, etc.) are also present. Catalysts are dehydrating agents for the carbonific compound: acid-forming salts which form acid *in situ* at a temperature lower than the decomposition temperature of the carbonific compound are generally used. Carbonifics are monomeric or polymeric polyhydroxylated compounds (e.g., sugars, urea/formaldehyde condensation products, etc.) which are capable of forming strong chars. Spumifics are compounds which evolve large quantities of nonflammable gases (e.g.,melamine, guanidine, urea, etc.). The decomposition temperature of the spumific must correspond to the temperature of dehydration/char formation of the carbonific. Mixtures of spumifics can be used to provide gas evolution over a broader temperature range. The necessary synchronization of reactions and other requirements for intumescence are quite complex (Roth and Green, 1974) and much work is in progress on improved technology. The protection of flammable plastic substrates with intumescent coatings has been proposed recently (Slysh, 1974), although, traditionally, intumescent coatings have been used primarily or exclusively for cellulosic substrates such as wood and fiberboard.

Nonconventional intumescent coatings are, by definition, those in which the key elements of intumescence are incorporated into the resin binder. Triphenyl phosphite modified epoxy coatings (Blair et al., 1972), and clear intumescent polyurethane coatings (Clark et al., 1967) are among compositions documented.

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