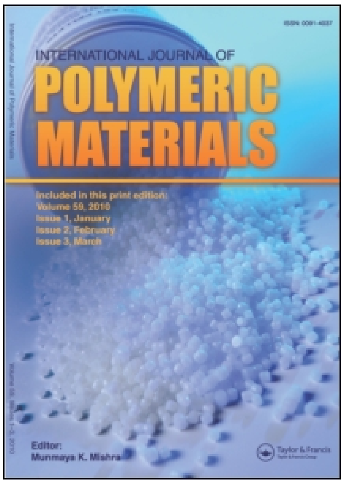

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Flammability Aspects of Foams†

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The growth of both flexible and rigid foams in the last decade has been very spectacular due to a combination of factors such as light weight, excellent physical properties and relatively low costs. The wide acceptance of foams in many diversified industries has led to the necessity of developing foams of low combustibility, often combined with low smoke evolution in case of fire, particularly in industries such as building and construction, transportation, bedding, etc. This paper deals with commonly used methods to impart varying degrees of flame retardance to foams and discusses effects of elemental constituents, synergism, fillers as well as some more recent approaches in changing the chemical structure to yield foams with inherent low combustibility and low smoke. Methods for incorporating flame retardants are reviewed. Finally, some aspects of government and code regulations concerning plastic foams are briefly discussed.

INTRODUCTION

The growth of cellular plastics in the last decade has been quite spectacular. This is borne out by the statistics shown in Table I.[1] The largest segments of organic foams are polyurethane, polystyrene, polyvinyl chloride and polyolefin foams although many other types of foams such as phenolic, epoxy, ABS, "Noryl", polycarbonate, etc. are used in speciality applications. The uses of cellular plastics, both flexible and rigid, apply to many industries, in particular the transportation, bedding, furniture, building and construction, appliances, packaging, carpeting (underlay and flooring) and other industries. A breakdown of the use of foams in some of these industries is shown in Table II.[2] A relatively large amount of unfavorable publicity has appeared in the news media on the combustion, smoke and toxicity aspects of foams. Some of these news reports or television presentations gave accounts of hazards of foams during fires which were often blown out of proportion or did not make a

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†The term "flame retardant" as it appears in the text is a relative term and is not intended to reflect hazards presented by foams containing those products or any other under actual fire conditions.

TABLE I

Summary of U.S. foam markets[a]

	Millions of pounds				
	1972	1975	1976	1977	1980
Rigid urethane	250	340	373	409	519
Flexible urethane	810	1,044	1,126	1,138	1,627
Polystyrene[b]	285 (535)	363	380 (670)	410	490 (900)
PVC	304	515	560	603	690
Total	1,649	2,262	2,439	2,560	3,326

[a] Source: Data from *U.S. Foamed Plastics Markets & Directory 1977*, Technomic Publishing Company, Westport, Conn.

[b] Includes expandable beads and Styrofoam®

Figures in parentheses include foam sheets.

TABLE II

Summary of U.S. foamed plastics markets[a]

	Millions of pounds				
	1972	1975	1976	1977	1980
Furniture	452	617	659	670	907
Transportation	329	436	470	479	680
Bedding	110	142	153	160	207
Carpet underlay and flooring	154	213	235	251	310
Textile	19	76	88	95	122
Packaging	214	267	274	296	353
Construction	143	198	221	241	291
Tanks/pipe	32	44	48	53	70
Appliances	51	70	77	84	113
Marine	22	29	31	34	41
Miscellaneous	52	100	88	116	132
Total	1,578	2,192	2,344	2,479	3,226

[a] Source: *U.S. Foamed Plastics Markets & Directory 1977*, Technomic Publishing Company, Westport, Conn.

serious effort of comparing hazards of more conventional building materials such as wood with foam plastics during a fire.

The lower density of cellular plastics or plastic foam as compared to bulk materials is responsible for the relatively low fuel contribution on a volume basis. However, the lower density in foams results in a larger surface area which makes the problem of combustion more acute than it is in bulk polymers. The combustion of organic foams is dependent on a number of chemical, physical and geometrical factors (cell geometry). Among the chemical factors should be mentioned the chemical structure of the polymer itself, the presence of aromatic, heterocyclic, or other chain stiffening groups or polar groups (which raise the T_g of the polymer), the functionality of the polymer components, the presence or absence of crosslinking (thermoplastic vs. thermosetting) and the degree of crosslinking. The physical factors include density, thermal stability and the ease of combustion of the thermal degradation products. As with bulk polymers the combustion of foamed polymers depends upon the sum of all the energy factors of the molecule. The most important of these energy factors relating to combustibility are cohesive energy, bond dissociation energy and heat of combustion.[2-5]

Geometrical factors include the cell geometry, i.e. the shape and size of cells as well as open or interconnecting vs. closed cells. The burning rates in open-celled foams are generally much higher than in closed-cell foams since the large internal surfaces in the former contact air directly. Obviously, the nature of the blowing agent within the closed cells will have some influence on the combustion of foams. In addition, shape and thickness of the foam will have some bearing on the burning rate. Certain silicone surfactants have been reported to have a beneficial effect on both flammability and smoke evolution.[6-8]

GENERAL METHODS OF FLAME RETARDANCE IN POLYMERS

At any time during burning of a polymer, there is a vapor phase in which flame reactions are occurring and a condensed phase or surface in which fuel for the gas reactions is being produced.

Hence, there appear to be two fundamental approaches in changing the flammability of polymers by chemical means. The course of reactions in the condensed phase may be modified either to decrease the amount of volatile degradation products or to prevent burning in the gas phase. In the former case, this can be accomplished by increasing the thermal stability of the polymer or changing the course of the thermal degradation. In the latter case the mixture of fuel and air may be diluted with an inert, non-combustible gas. Other methods would be the cooling of the fuel by some endothermic reaction or introducing some material to inhibit free radical reactions involved in the flame formation and propagation.

In agreement with these general theories, approaches toward reducing the flammability of polymer systems can be grouped into several categories[9]:

1) Dilution of the polymer with non-flammable materials, e.g. inorganic fillers.

2) Incorporation of materials which decompose, when heated, to give non-flammable gases such as carbon dioxide.

3) Addition of flame retardants which catalyze char rather than flammable product formation.

4) Design of polymer structures which favor char formation.

5) Incorporation of materials to terminate the free radical chain reactions which occur during combustion.

6) Formulation of products which decompose thermally with a net endothermic reaction.

EFFECT OF ELEMENTAL CONSTITUENTS

As is the case with bulk polymers, a variety of compounds containing elements in Group V of the Periodic Table of Elements (nitrogen, phosphorus, arsenic, antimony and bismuth) and Group V (fluorine, chlorine, bromine and iodine) exhibit flame retarding action in cellular plastics. Of these phosphorus, bromine, chlorine and antimony (preferably as oxide) are considered to be the most efficient flame retardant elements. Boron compounds are also known to impart good flame retardant action to foams. The mechanism of the effects of these elements during combustion has been reported by a number of investigators[2,10–13] and no effort will be made here to describe them in detail. These elements are of course available in many different forms, and their flame retardant action depends upon the chemical nature of the compound containing that particular flame retardant element. Phosphorus-containing flame retardants, for instance, are marketed among others in the form of phosphates, phosphonates, phosphites, phosphonium, phosphonitrilic, aminophosphonates, phosphines, phosphine oxides, etc.[2,14,15] Significant differences in the performances of phosphates, phosphonates and phosphites in the flame retardance of some urethane and isocyanurate foams have been reported by Papa and Proops[16] and Kresta and Frisch.[17] It should be pointed out that while phosphorus is perhaps the most effective flame retardant element in a number of foam systems, many phosphorus-containing compounds are susceptible to hydrolysis. Likewise, certain boron-containing flame retardants experience the same difficulties. Hence, exposure to humid aging conditions may result in reduced effectiveness in flame-retardance. In addition, many phosphorus-containing flame retardants may reduce the thermal stability of the foam systems.

While halogens and phosphorus, alone or in combination with each other or in conjunction with other elements are very effective with regard to lowering the combustibility of foams, they generally enhance the smoke evolution during combustion. In addition, the gases produced during the combustion of foams containing flame retardants may produce corrosive vapors (e.g. HCl or HBr) as well as vapors which may present certain health hazards. However, without going too deeply into the sensitive subject of toxicity, it can be stated that it has been found that anoxia (insufficient oxygen) due both to oxygen consumption by the fire and to carboxyhemoglobin saturation of the blood from inhalation of carbon monoxide is the leading cause of fire deaths.[18-21] Besides antimony trioxide, other inorganic salts such as zinc borate, ammonium phosphate, magnesium ammonium phosphate, potassium fluoroborate, alumina hydrate, etc. either alone or in combination with other materials have been reported to be effective in various foam systems.[2,14,23]

SYNERGISM

Synergism plays an important role in lowering the combustibility of foams. In particular, the flame retardant effectiveness of halogen-containing compounds can be enhanced with synergists of several types, especially

1) inorganic oxides, sulfides (notably antimony trioxide), or other salts,
2) phosphorus (organic and inorganic compounds), and
3) free radical initiators.

There are many examples cited in literature of the synergism between halogen-containing compounds and antimony trioxide in polystyrene, polyolefin, polyurethane and PVC foams.[2,10,15,24,25]

Phosphorus-halogen synergism has been reported in many foam systems[2,14,26,27] particularly in flexible and rigid urethane foams.

The synergism between halogens and free radical initiators such as peroxides, hydroperoxides, etc. has been reported by Eichhorn[10] and Ingram.[29]

The mechanism of the synergistic action of flame retardants has been described by a number of investigators.[2,10,12,14,28]

Phosphorus-nitrogen synergism in foam systems was described by Robitschek.[30]

The combined effects of ternary systems such as phosphorus/antimony/halogen and phosphorus/halogen/nitrogen have been reviewed by Tesoro.[31]

A number of investigators have seriously questioned whether "real" synergism is present in all the cases reported in literature. Kresta and Frisch[17] have clearly demonstrated a case in which an apparent synergism occurred in various urethane foam systems containing phosphorus and chlorine using oxygen index data. However, by taking into account the correct relationships of phosphorus and chlorine with oxygen index, no actual synergism could be detected in these foam systems. Weil[28] has analyzed critically many data of apparent synergism in an excellent review. He concluded that while certain synergisms such as combinations of antimony and halogens are valid, other types of "synergism" such as halogen and phosphorus appear to be of questionable reality. Synergism of halogen additives by peroxides and other free radical generating compounds appear to be the result of melt viscosity depression and dripping.[32,33] This effect may not contribute to fire safety if the dripping material continues to burn. Hence, the appearance of synergism can often be merely the artifact of a nonlinear response-concentration relationship.[28]

A number of very good reviews and books have appeared within the last few years dealing with some aspects of flame retardancy and smoke evolution in various foam systems.[2,5,14,15,33]

EFFECT OF "INERT" FILLERS

A large number of various fillers, primarily inorganic, either in form of solid particles, microspheres or fibers, have been employed in many different foam systems. In addition to changing some of the physical properties of the foams (e.g. density, compressive strength, etc.), they may affect the combustibility of foams, either positively or negatively. A number of inorganic fillers such as alumina hydrate, calcium carbonate, glass fibers, and others are effective in some foam systems. However, it is difficult and often inaccurate to make broad generalization as to the effectiveness of these fillers. For instance the addition of glass fibers to some thermoplastic materials increases the combustibility since it often prevents dripping of molten particles. This dripping phenomenon is actually held responsible for lowering the combustibility since it removes the flame away from the main body of the polymer.[53] On the other hand, the addition of glass fibers to urethane foam, particularly in combination with halogen-containing flame retardants results not only in significant improvement in strength properties but also in lower combustibility.[54,55]

Other fillers such as sand have been reported to be effective in conjunction with organic flame retardants in various foam systems.[56–58] It is interesting to note that the flammability seems to vary with particle size of the sand, the coarser variety being more effective.[58]

OTHER APPROACHES OF LOWERING COMBUSTION IN FOAMS

In addition to the conventional approaches of lowering the combustion of the most commonly used foams, many efforts have been made to incorporate chemical structures different from the chemical structure of the base polymer, which inherently impart either high thermal resistance, improved flame retardance, and in some instances reduced smoke evolution. This concept, due to economic considerations, is only of academic interest for foam systems such as polystyrene or polyolefin foams—at least at present; however, it is an increasingly important one in the field of urethane or other isocyanate-based foams. In this case, selective catalysis of the isocyanate group has enabled the foam industry to produce foams containing more thermal resistant groups than the urethane group i.e. by formation of isocyanurate, oxazolidone, cyclic imides, and carbodiimide groups or containing a combination of these groups.[8,17,36–38] The preparation of isocyanurate and carbodiimide groups is based solely on the selective catalysis of isocyanates while the formation of oxazolidone and cyclic imides involves the reaction of isocyanates with epoxides or acid anhydrides employing specific catalyst systems, respectively, as seen in the equations in Figure 1. Urethane-modified isocyanurate foams have gained the widest commercial acceptance among the rigid modified isocyanate-based foams. This is due to the fact that the isocyanurate group generally imparts improved heat stability, lower combustibility and less smoke evolution as compared to unmodified urethane foams.

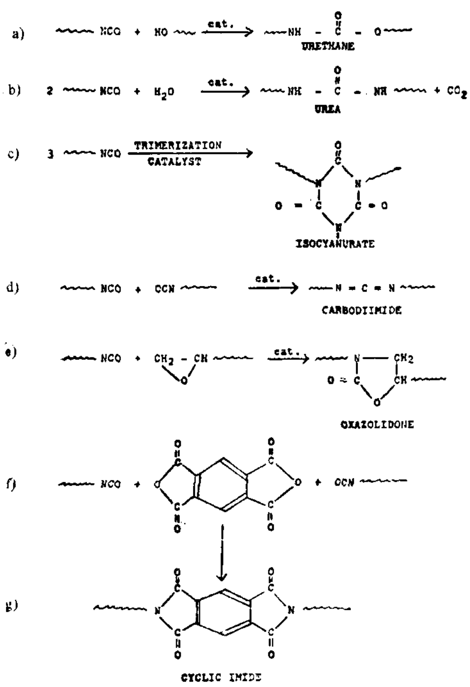

FIGURE 1 Some reactions of Isocyanates in foam formation.

A number of miscellaneous materials have been reported to be effective both as flame retardants as well as smoke suppressants in foam systems either alone or in combination with other flame-retardants. Typical examples are bis-(cyclopentadienyl) iron (ferrocene),[49] potassium borofluorate[50,51] and certain dibasic acids or anhydrides, e.g. fumaric acid.[52]

METHODS FOR INCORPORATING FLAME RETARDANTS

The methods for incorporating flame retardants include the following:

1) The use of non-reactive flame retardant additives. These can be either organic or inorganic compounds. Examples of the former are tris (2, 3-dibromopropyl) phosphate, chlorinated paraffins, and brominated alicyclic compounds. Typical inorganic additives are zinc borate, aluminium oxide trihydrate, antimony oxide, etc.

2) Incorporating reactive flame retardant components into the polymer molecule—typical examples are phosphorus and/or halogen-containing polyols, chlorendic anhydride, brominated bisphenol A, etc.

3) The use of flame retardant coatings, e.g. intumescent or cementitious coatings.

The selection of a particular method for incorporating flame retardants into cellular plastics depends upon the type of polymer and the end use requirements. In many cases, such as in rigid urethane foams for insulation in building applications, reactive components which become part of the polymer molecule, have been found to be preferable to non-reactive additives, particularly from the standpoint of permanence properties. In the case of non-reactive flame retardants, there always exists the possibility of extraction by solvents or water or by migration of the additive. Nevertheless, the additive type of flame retardant is preferred in certain types of foams such as polyolefin or polystyrene foams. The reason for using "inert" additive type rather than reactive flame retardants is the danger of modifying drastically certain properties such as strength, electrical properties and thermal stability. In addition, the processing characteristics may be significantly changed and last but not least is the cost factor which has to be considered.

The use of flame retardant intumescent coatings for foams is effective in some applications, but often may not be adequate to meet certain specifications and building codes.

Very recently Nadeau *et al.*[35] reported on the effects of two types of spray-on coatings over rigid urethane foams of various flame spread ratings which underwent a series of fire tests conducted in the Factory Mutual Research

Corporation's 25 foot high factory-like open corner wall facility and in the Underwriters Laboratories' 8 foot high residential-like enclosed corner wall facility. The two spray-on coatings were a lightweight magnesium oxychloride-based cementitious material, and the other was based on a modified fiber-reinforced gypsum-based cementitious material. The results from these tests indicated that combustible rigid spray-on urethane foam can be effectively protected with cementitious coatings of the type investigated at thicknesses ranging from one-quarter to one-half inch. The degree of protection was proportional to the thickness of coating and to a lesser degree on the combustibility rating of the foam. Furthermore, the two coatings performed equally well at similar thicknesses. This finding is not too surprising considering that the mechanism of protection for each coating is based on the endothermic heat of vaporization of the water of hydration.

GOVERNMENT AND CODE REGULATIONS CONCERNING PLASTIC FOAMS

In the following, only some aspects of government action and code regulations with regard to foam plastics, either in force, or pending, will be briefly discussed. In 1973, the Federal Trade Commission brought a suit against twenty-five companies and the Society of the Plastics Industry (SPI) alleging that the labeling of foams as self-extinguishing, flame proof etc. constituted a misrepresentation to the public since certain laboratory tests such as ASTM D-1692 or even certain larger scale tests such as ASTM E-84 (the Steiner tunnel test) did not reflect hazards under actual fire conditions.

In 1974 a Consent Agreement was entered into by the Federal Trade Commission and the above respondents. It is important to note that the FTC Consent Order did not in any sense ban, restrict or prohibit the use of any plastic in any application. However, the FTC Order did define rules to be followed in the advertising and promotion of the use of cellular plastics.

Perhaps the most significant result of the Consent Order was the establishment of a Product Research Committee in November 1974 with the task of coordinating and managing a scientific research program on the combustibility of cellular plastics for a period of five years. A $5,000,000 Program Fund was established to finance this program which was funded by assessment of the respondents.

The objectives of the Committee's research program were defined as follows:

1) "Determine the most effective manner for employing cellular plastics products and systems containing such products to minimize fire hazards in the final intended uses."

2) "Develop guidelines for the effective use of such cellular plastics."

3) "Develop tests or the basis for standards, including large-scale tests as well as methods by which the results of small-scale tests can be correlated to provide an index of the behavior of cellular plastics in various burning conditions, which tests accurately relate to real fires."

The research program was directed specifically toward four distinct areas:

1) Fundamental research
2) Small-scale tests
3) Large-scale tests
4) Combustion product toxicity

The Products Research Committee is also establishing a materials bank of 18 different generic foams in two sizes in order to provide standardized samples for fire research. In addition to the research program proposed by the Products Research Committee, awards were approved for three research programs proposed by the Society of Plastics Industry (SPI) for credit against the 1977 assessment.

It should also be pointed out that prior to the FTC action in 1973, the Cellular Plastics Division of the Society of Plastics Industry had proposed in 1965 that the industry fund a multi-phase research program. The first phase of this program, sponsored by SPI and conducted by Factory Mutual Research and Underwriters Laboratories consisted of a study to collect and review data from actual fires involving cellular plastics and to evaluate existing test procedures to determine their relevance and correlation to actual fire behavior.

The second phase of this study conducted by the Illinois Institute of Technology Research Institute, involved the selection of the most critical specific use applications for further study, and the design of large-scale tests which represented those applications. Phases three and four consisted of the actual testing carried out by Factory Mutual which reached an agreement with the SPI Combustibility Committee to construct a large-scale corner wall. Actual fire testing began in early 1972. The goals of this program were and still are:

1) Definition of the combustibility behavior of rigid cellular plastics when used as wall and ceiling insulation in large room spaces such as factories or warehouses.

2) Determination of the adequacy or inadequacy of code specifications and current combustibility tests.

3) Development and verification of new tests which relate to large-scale tests which are more representative of realistic fire situations.

This testing program was well underway when the FTC lodged their complaint that resulted in the Consent Agreement in 1974.

Recently new regulations concerning foamed plastics have been incorporated into three model building codes: International Conference of Building Officials (ICBO), Uniform Building Code; Building Officials and Code Administrators (BOCA), Basic Building Code; and Southern Building Code Conference (SBCC), Standard Building Code. These regulations deal with the safe-use applications of foams with regard to fire safety. Some of the key points of these regulations are the elimination of the use of exposed foam and the requirement that foams be protected with thermal barriers such as gypsum board or similar materials and the "diversified testing" provision. The latter means that if a foam product does not fall under any specific provision of the new code, the product may be accepted for the intended use on the basis of satisfactory performance in large-scale testing. Among the "diversified tests" which are being promulgated is the Compartment Corner Combustibility Test which was developed by Underwriters Laboratories, Inc. (UL)(59) which is used to evaluate the behavior of wall structures typical of residential construction during a fire. Extensive test results were recently reported by Condit and Cianciolo[60] and Cianciolo and Robertson.[61] Currently, a small-scale corner test method reported previously by Nadeau and Waszeciak[62] is being considered for adoption by ASTM.

While most of the publicity on the combustibility of foams is concentrated on rigid foams for insulation of buildings, increasing concern has also been expressed in recent years over the combustibility of flexible foams in bedding, upholstered furniture and carpet underlay. The State of California has been a leader in areas of consumer flammability legislation and development of flammability test methods. A flammability requirement for mattresses became law in California in September 1970,[63,64] and performance standards were issued by the Bureau of Home Furnishings in January 1973.[65,66] At present, there is no national flammability standard for upholstered furniture, but the National Bureau of Standards is currently formulating a proposed standard which is expected to be published in the near future. A considerable amount of research on flexible foam in home furnishing applications has been conducted in England at the Rubber & Plastic Research Association (RAPRA) and the Fire College at Moreton-in-Marsh as well as in the U.S. by the Southwest Research Institute.[67] Several reports on their findings using various test methods are now available which will undoubtedly serve as guidelines with regard to future government regulations.

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