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New polymeric compositions for nonflammable and thermally stable foams

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Rice University, 1992
RICE UNIVERSITY

NEW POLYMERIC COMPOSITIONS FOR NONFLAMMABLE
AND THERMALLY STABLE FOAMS

by
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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
MASTER OF SCIENCE

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ABSTRACT

NEW POLYMERIC COMPOSITIONS FOR NONFLAMMABLE AND THERMALLY STABLE FOAMS

by FABIO BRAVO

There is a great need to develop new polymer foam systems that combine the advantages of polyurethane foams (low cost, ease of processing, desirable physical properties) with nonflammability and thermal stability which polyurethanes lack. In this project we address this need by synthesizing novel polymer networks with a substantial content of nonflammable elements. Specifically most of the pendant hydrogens have been eliminated (or replaced with fluorine), and a substantial fraction of the carbon atoms are replaced with oxygen, phosphorus, and nitrogen. Other elements such as Ca, Mg, Al, Sb, V, and B are also incorporated in the polymer network to enhance nonflammability. The selected phosphorus compounds are in their highest oxidation state (+5) and the nitrogen is present in the form of five or six-member heterocyclic rings. Following these guidelines, several rigid, semi-rigid, and flexible, foamed-in-place foams with outstanding nonflammability and thermal stability have been developed.
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to the following persons:

Dr. C.D. Armeniades for serving as my thesis advisor, for his insight and guidance in directing this research, and for many helpful discussions and suggestions.

Mr. Gus Nichols for his frequent fruitful discussions and constructive suggestions regarding formulations and methods.

Dr. S. Hwu for serving in the oral examination committee and for the use of the TGA equipment.

Dr. C.A. Miller and Dr. K. Zygourakis for serving on the oral examination committee.

My wife, Delia, for her constant support and encouragement, her patience, and her help typing this thesis.
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I. INTRODUCTION

A. Polymeric Foams

In general terms a foam is formed when gas bubbles are dispersed in a liquid matrix. If the liquid subsequently solidifies the foam becomes permanent. The most common permanent foams have matrices, consisting of polymeric materials. Low density foams are dispersions of relatively large volumes of gas in relatively small quantities of polymer. These foams are usually produced by processes which involve the formation of polymer networks with simultaneous nucleation and growth of gas bubbles.

Open-cell foams correspond to the case in which the gas is a continuous phase; closed-cell foam is the case in which the gas is a dispersed phase (no "communication" between the gas bubbles).

The main applications for polymeric foams are in the furniture, transportation, construction and footwear industries, as well as in thermal insulation and in shipping containers.

Flexible closed-cell foams are made mainly from polyethylene (PE), plasticized polyvinyl chloride (PVC), and polyurethane (PUR). PUR open-cell foams are extensively used in the upholstery and bedding industries due to their outstanding resiliency and cushioning characteristics. However, all of these foams have a serious drawback: they are highly flammable; when exposed to flame they ignite easily and burn rapidly with evolution of black smoke and toxic gases (HCN and CO from PUR, HCl from PVC, etc.). The
use of flame retardants (especially common for PUR), as additives or incorporated in the polymer chains produces only small reductions in flammability with usually dramatic deterioration of the foam properties (increase in density, decrease in flexibility or strength) while maintaining (or even increasing) the production of toxic gases due to thermal degradation.

Some inherently nonflammable foams (polybenzimidazoles, polyimides, etc.) have been produced (even commercially) but their high costs, difficult production, and relatively poor resiliency and cushioning properties place severe limits on their applications.

B- Importance of Nonflammable Foams

After thousands of years of attempts to control fire by human beings, there are still too many deaths due to accidental fires. These deaths are caused not only by fires produced from spectacular plane or car crashes but also by fires accidentally initiated with matches or smokers' materials. (1). It was estimated that in the seventies about 12,000 people died every year and several million people were injured as a result of various fires (2).

However, an appreciable number of these deaths could have been avoided by the use of nonflammable materials (especially nonflammable polymers). The development of nonflammable foams (the topic of this research) has very promising applications: these include sophisticated aerospace or naval applications, thermal insulation, furniture, etc.
As an example, 496 out of 2,727 human deaths in U.S. air accidents between 1965 and 1978 were due to the effects of fire and smoke (3). The investigations of these accidents have shown that many of these deaths could have been avoided by the use of nonflammable materials in aircraft cabins.

Furniture and upholstery foams are involved in many residential fire deaths. Most of these fire deaths are not produced in big fires involving buildings, factories or many houses (4,5); the greatest number of fire deaths in the U.S. are due to fires which occur in one and two family residences (4,5). As many as 95% (6) of the fire fatalities occur in residences. It is not clear if the most common cause of residential fires is heating and cooking (4,5) or cigarettes(6), but the fires responsible for the largest percentage of fire deaths in U.S. as well as in Canada and U.K. (4) are initiated by cigarette ignition of upholstered furniture and bedding (4,5). It has been estimated that in the U.S. in 1984 cigarette/soft furniture fire accidents produced 49,000 residential structural fires which resulted in 1,530 deaths, 3,950 injuries and U.S. $ 320 millions in damages (7). This amounts to 36% of all residential fire deaths and 19% of the injuries (7).

In another study, covering the period 1980 to 1983, upholstered furniture accounted for 25% of the first items ignited in fatal residential fires (7). Finally, another study shows that 80% of the fire victims die from smoke inhalation rather than burns (7).

Most of the upholstered furniture manufactured today contains some type of flexible polyurethane (PUR) foam (4,8). More than 3 million tons of polyurethane (6,8) are used yearly in: furniture and mattresses (about
32% of the total world production (8), transportation, building, leisure, and shoe industries (4,8). However, as mentioned before, PUR foams have a very serious drawback for many applications: they are highly flammable, ignite easily and burn rapidly with the evolution of smoke, and highly toxic gases. It has been proved that the use of this material has produced (or contributed to) serious injury and loss of life in building, aircraft, automobile, and spacecraft cabin fires.

According to these data, the importance of developing and producing fire resistant and thermally stable foams, for upholstered furniture and other uses in automobiles, aircraft and spacecraft is quite obvious. In this work we shall use the term "nonflammable" to identify materials that will not ignite and sustain combustion under their usage conditions.

C- Research Objectives

The purpose of this research is to develop chemical formulations for inherently nonflammable and thermally stable foams.

D- Foam Requirements

In addition to nonflammability and thermal stability the new foams must meet several requirements for ease of production and to better fulfill their intended uses:
1) Since there is a lot of commercial equipment designed for PUR foams, which use two-component liquid systems that are mixed and foamed-* in-place, it would be a great advantage if the new, nonflammable foams could utilize existing equipment with only minor modifications. Consequently:
   a) The foam precursors should be liquids or low-melting solids at ambient temperatures.
   b) They should have acceptable shelf lives (at least 12-months stability at ambient temperature storage) and should not require special storage conditions.
   c) They should be (relatively) non toxic and non corrosive.
   d) Foaming reactions should be tolerant to small deviations in conditions (stoichiometry, temperature, etc.).
   e) The foaming reaction should not produce dangerous amounts of flammable or toxic gases.

2) Since the potential applications of these foams cover a wide range from packaging, to furniture, to thermal insulation, to sophisticated naval and aerospace applications, the resulting nonflammable foam systems should be capable of yielding foams with a range of physical properties: density should range from 10 to 100 Kg/m³; tensile strength from 20 to 200 KPa; it is also desirable to formulate systems with both open-cell and closed-cell structures, the latter for use as thermal insulation.

---

* Foam-in-place techniques achieve rapid formation of PUR foam by mixing "in-situ" two liquid components (isocyanates and polyols) which react rapidly and exothermally to produce a polymer network. Foaming is achieved by the flashing of low-boiling additives (foaming agents) or from the generation of carbon dioxide when water is present in the reaction system.
E- Proposed Approach

Most current foams consist of polymer chain networks that are composed almost exclusively of carbon and hydrogen. Since both of these elements are highly combustible it is not surprising that the current foams are highly flammable. In view of the lack of success that traditional approaches with fire retardant additives have had on foams, we use in this project a completely new approach: we eliminate most pendant hydrogens or replace them with fluorine, which is nonflammable; within the chain we replace a substantial fraction of the carbon atoms with other elements: oxygen, phosphorus, and nitrogen. These three elements are the most used in this work. Fluorine is used only if completely necessary due to the high cost of its compounds. Other elements such as Ca, Mg, Al, Sb, V, B are also used to enhance nonflammability.

This approach is completely innovative not only because most of the previous work in nonflammable foams has tried to improve the nonflammability of known foams (especially PUR) or the foamability of nonflammable polymers, but because the above mentioned elements are not traditional in polymer production. This approach could appear more than innovative and ambitious: It could appear completely wrong. In fact, to work with elements different to C seems too ambitious, especially considering the statement by Allcock (9) "Nearly all polymer Chemistry to date has revolved around the chemistry of one element: Carbon".

To replace C by other elements for achieving nonflammability sounds reasonable. But to choose as "best" the elements P, O and even N seems
illogical and wrong. Everybody knows that the element phosphorus is an
incendiary and for that reason it is used in matches. Oxygen is also
required to support fire. So, two of the components of the classical
triangle of fire, the source and the oxygen, are two out of the three
proposed elements for achieving nonflammability. Nitrogen is also not
traditional as a flame retardant. The explanation for this paradox is
simple: It is not the elements themselves, but their chemical state in the
compounds they form, which provides their characteristics (in this case the
nonflammability) of the compounds. The example is obvious: C is
flammable in hydrocarbons and most other organic compounds, but in its
highest oxidation state (as CO$_2$) is used as a fire extinguisher, because CO$_2$
cannot be further oxidized. Similarly, phosphorus in its highest oxidation
state (+5) is a powerful fire retardant: for example, when 3 moles of
methyl alcohol (a fuel) are reacted with one mole of phosphoric acid, the
product, trimethyl phosphate, is completely nonflammable. Consequently
we have selected certain special phosphorous compounds (with its highest
valence: +5) to work with. Similarly, for achieving fire retardance as well
as thermal stability with nitrogen, we introduce it in our polymer
networks in the form of 5 or 6 member heterocyclic structures. We will
call this type of N "high-quality nitrogen".
II- LITERATURE REVIEW: FLAMMABILITY AND THERMAL STABILITY

A- Methods for Decreasing Polymer Flammability

Efforts to develop nonflammable foams are not new. Many studies have been made in this topic. In general, there are three different approaches to the problem:

1) To improve the nonflammability of known flammable polymers (especially PUR), using additives (flame retardants).

2) To make foamable the known nonflammable polymers.

3) To develop new foamable and nonflammable polymeric materials.

1) Fire-Retardant Additives

The use of fire-retardants seems to be the easiest way to decrease the inherent flammability of common polymers and, consequently, it is the most traveled one. Flame retardants are the second most used additives (after plasticizers) in polymers (10). Most flame retardant systems use either chlorine or bromine, phosphorous, boron and antimony compounds (11,12,13). Reference (14) lists 154 commercial flame retardants for flexible PUR and 143 flame retardants for rigid PUR.
With the above mentioned flame-retardant additives the PUR becomes more difficult to ignite and/or less likely to support flame (11).

Table II-1 (8) lists several flame retardants commonly used with PUR, and states the type of product (non-reactive liquid, reactive additive, filler) and method of usage. These flame-retardants include:

a) Antimony trioxide \((\text{Sb}_2\text{O}_3)\) (14,15) or the mixture antimony trioxide with halogenated flame retardants (brominated or chlorinated compounds) (15,16,17).

b) Different halogenated compounds (especially brominated compounds), such as: Tribromocumene (18,19), dibromoethyl-dibromocyclohexane (commercially available as SAYTEX BCL-462 from Ethyl (20)), Hexabromocyclododecane (commercially available as FR-1206 from Ameribrom, SAYTEX HBCD from Ethyl and CD-75P and SP-75 from Great Lakes Chem.) (14), pentabromodiphenyloxide (trade names: FYROL PBR from AKZO, FR-1205 and 1215 from Ameribrom, Electrofine S-70 from Atochem and DE71 and DE60F Special from Great Lakes Chem.) (14), tetrabromodiphenoxybenzene (commercially available as SAYTEX 120 from Ethyl (20), Decabromodiphenyloxide (FR-1210 from Ameribrom, Thermoguard 505 from Atochem, SAYTEX 102 and 120E from Ethyl and DE-83R from Great Lakes Chem.) (14), diester/ether diol of Tetrabromophtalic Anhydride (commercially : SAYTEX RB-79 from Ethyl) (20), Tribromoneopentyl alcohol (FR-513, Ameribrom) (14) and Dibromoneopentyl glycol (FR-522 from Ameribrom and FR-1138 from Ethyl), Octabromodiphenyl oxide (FR-1208 from Ameribrom, SAYTEX 111 from Ethyl and DE-79 from Great Lakes Chem.)(14), brominated
### Table II-1: Some Flame-Retardants for Polyurethanes.

<table>
<thead>
<tr>
<th>A. Non-reactive liquids</th>
<th></th>
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<tbody>
<tr>
<td>Tris (2-chloropropyl) phosphate, ‘Daltogard’ F</td>
<td>All polyurethane foams including polyester-based foams and microcellular elastomers.</td>
</tr>
<tr>
<td>Tris (2-chloroethyl) phosphate, (T.C.E.P.)</td>
<td>Polyether-based flexible and rigid foams.</td>
</tr>
<tr>
<td>Tris (2,3-dichloropropyl) phosphate, ‘Fyrol’ FR 2</td>
<td>Polyether-based rigid and flexible foams.</td>
</tr>
<tr>
<td>‘Cellulfex’ FR-2</td>
<td></td>
</tr>
<tr>
<td>Tetrakis (2-chloroethyl)-2,2-bis-(chloromethyl) propylene-phosphonate. ‘Phosgard’ 2XC02</td>
<td>Low volatility material for flexible and rigid foams.</td>
</tr>
<tr>
<td>Dimethyl methyl phosphonate</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B. Isocyanate-reactive additives</th>
<th></th>
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<tbody>
<tr>
<td>Tris (polyoxyalkylene glycol)-phosphonates and phosphate esters.</td>
<td>Flexible and semi-rigid foams.</td>
</tr>
<tr>
<td>Tris (halogenated polyol)-phosphonates.</td>
<td></td>
</tr>
<tr>
<td>Dibromoneopentyl glycol. ‘FR’ 1138</td>
<td>Flexible and rigid foams.</td>
</tr>
<tr>
<td>Brominated polyester and polyether diols. ‘Saytech’ RB-79 and 42-43</td>
<td>Polyether-based polyurethanes.</td>
</tr>
<tr>
<td>Tetrabromobisphenol A</td>
<td>Rigid polyurethane and polyisocyanurate foams.</td>
</tr>
<tr>
<td>Tetrabromophthalic anhydride</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>C. Fillers</th>
<th></th>
</tr>
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<tbody>
<tr>
<td>Ammonium salts, sulphate, polyphosphate, etc.</td>
<td>Together with halogenated additives in rigid polyurethanes.</td>
</tr>
<tr>
<td>Aluminium hydroxide. Melamine.</td>
<td>All polyurethanes but especially in low density flexible foams for ignition and smoke suppression.</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>Heat absorbing filler.</td>
</tr>
</tbody>
</table>
alkyd resins (21), halogenated hydroxyl-containing derivatives of pentaerythritol (22), halogen-containing dicarboxylic acid anhydride (23,24), brominated diols (25), different brominated organic products (commercially available from Atochem, Ethyl, Ferro and Pearsall) (14), neopentyl bromines prepared by reactions of pentaerythritol with hydrogen bromine (26), mixtures of tetrabromophtalic anhydride derivatives (typically 45% bromine or Chlorine containing phosphate esters) (27), halogenated aliphatic compounds (commercially available as Bromoklor 50 and Bromoklor 70 from Ferro Chemicals (28,14) and DD-8119 from Dover (14)); halogenated hydrocarbons (from Atochem, Dover, Ferro, Harwick and Occidental (14)) or halogenated hydrocarbon dispersions and too many other halogenated organic compounds (available from Atochem, Dover, Harwick, Occidental, Pearsall, Quantum and Stranchem (14)).

As mentioned before, the halogenated (especially brominated) compounds are commonly used with antimony trioxide due to their known synergistic effect (16,17,28).

c) Phosphorus compounds such as: Triaryl phosphates (KRONYTEX®), alkyl diaryl phosphates (Phosflex 362, 390 and 370 from AKZO and Santicizer 141, 148 from MONSANTO) (14), phosphate esters (commercially produced by AKZO, Albright & Wilson, FMC and MONSANTO)(14), cresyl diphenyl phosphate (trade name: Disflamoll DPK from Mobay), octyl diphenyl phosphate (Santicizer 141 from MONSANTO and Phosflex 362 from AKZO)(14), t-butyl phenyl diphenyl phosphate (commercially : Santicizer 154 from MONSANTO, Kronitex 100B and 200B from FMC and several grades of Phosflex from AKZO)(14), combinations of pentate salts and nitrogen-containing
phosphates (29,30), blends of pentabromodiphenyl oxide and phosphate ester (12), tricresyl phosphate (Lyndol XP plus, Pliabrac TCP and Kronitex TCP from AKZO, Albright & Wilson and FMC respectively) (14), triphenyl phosphate (commercially: Phosflex TPP, Kronitex TPP and Disflamoll TP from AKZO, FMC and Mobay respectively)(14), trixylenyl phosphate (Phosflex 179A from AKZO, Kronitex TXP from FMC and Pliabrac TXP from Albright & Wilson)(14), tri-isopropylphenyl-phosphate (commercially available from AKZO, FMC and Albright & Wilson)(14), Tris(betachloroethyl) phosphate (TCEP, FYROL CEF and TCEP from Mobay, AKZO and Focus Chem. respectively)(14), tris(chloropropyl) phosphate and Tris(dichloropropyl) phosphate commercially available from ACETO, AKZO and Albright & Wilson (14), phosphonate esters (DMMP from Focus Chem. and Antibleze 19, 1045 and DMMP from Albright & Wilson)(14), ammonium polyphosphates (commercially available from Albright & Wilson and MONSANTO)(14), Ammonium phosphate powder (available as Exolit 422 from Hoechst-Celanese) (31), combinations of phenol or melamine-formaldehyde condensates with pentaerythritol and ammonium phosphate (32).

d) Zinc borate (chemical formula $2\text{ZnO-3B}_2\text{O}_3-5\text{H}_2\text{O}$ (33,34)), used alone or with antimony trioxide or ATH (due to the synergistic effect (33)) and commercially available as Firebreak ZB (from U.S. Borax) (14,34), ZB-112, ZB-325, ZB-237, ZB-223 and ZB-467 from Climax (14), and Zinc borate dispersions (commercially available from Harwick) (14).
e) **Alumina trihydrate** (commonly known as ATH) with different particle sizes (commercially available with median particle sizes between 1.6 and 9.0 microns (35)).

ATH is one of the most studied and used flame retardants for PUR (13). The ATH can be used in 3 different ways (36), as follows:

1) Post-treatment saturation or coating.

2) By foam generation with water slurry of the ATH (for hydrophilic PUR foams).

3) By total incorporation of the ATH into the polyol involved in the foam formulation.

Variations of the first method (post-treatment and coating) used in conjunction with ATH, are as follows (36):

- Adding a halogenated synthetic rubber (37).
- Using neoprene latex (35,38,39).
- Dispersing the ATH in neoprene or poly(vinylidene chloride) latex (40).
- Using neoprene latex, sodium silicate and, optionally, sodium fluoro-silicate (41).
- Using CO$_2$H containing the ATH and polychloroprene latex and vulcanizing with MgO or ZnO (42).

For the second way of ATH use, there are also several patented possibilities, such as using the product prepared by reaction of NCO terminated polyoxyethylene polyols with aqueous slurries of:

- Alumina hydrate, boric acid and melamine (43).
- Alumina hydrate and ammonium phosphate (44).
- Alumina hydrate, ammonium polyphosphate and poly hydroxyl organic compounds such as starch (45).
- Alumina hydrate, ammonium polyphosphate and wood pulp (46).
- ATH (75-150 parts), phosphorus containing additives (2-30 parts) and a surfactant (47).

Foams with greatly improved fire retardance have been reported using hydrophilic foams with ATH and phosphorus based flame retardants.

There are also several patents regarding the use of ATH as a flame retardant filler for PUR (36), as follows:

- Using ATH alone (48).
- Using ATH in addition to other compounds such as KCl, K₂SO₄ or Mg(OH)₂ (49) or sodium silicate (50) or a salt of a phosphate or polyphosphate (50).
- Using coarse particles (350-700 μm) of alumina hydrate (51).
- Using polyhalogenated aromatic compounds, ATH and antimony oxide (52,53).
- Using ATH and tris (β-chloroethyl) phosphate (54).
- Using ATH and Sb₂O₃ in a base containing 2,3-dibromo-2-butene-1,4-diol (55).
- Adding up to 50% of ATH and/or melamine to the polyol (56).

So, as mentioned before, ATH has been used extensively with PUR in attempts to formulate nonflammable PUR foams. One of the advantages of the ATH is that it produces no dangerous combustion products. It has a high content of chemically combined water (34.6%), which will not react with cured PUR (36). However, when exposed to higher temperatures (or
when in contact with a flame front), ATH decomposes, liberating water, which absorbs a large amount of heat (280 cal g⁻¹ Al₂O₃-3H₂O)(36).

Another way to reduce the flammability of PUR is to use in their production isocyanurates, thus, obtaining products with low flammability (even without the addition of flame retardants)(27).

Also, the use of flame retardant polyols, which can involve phosphorus or chlorine (57) can produce relatively good results. Some flame retardant polyols are (57):
Diethyl-N,N- bis(2-hydroxyethyl) amino methyl phosphonate, bis(dipropylene glycol) phosphonate, as well as some commercial available polyols such as Isond FRP-8 (Upjohn), VC-611 (Mobil), Niax RO 350 (Union Carbide)(57), Saytex FR-1138 (Ethyl Corporation) which is a brominated polyol (58), etc. The most common chlorine-containing polyols are poly(trichloro oxybutylene) adduct of a carbohydrate, polyols based on chlorendic ahnydride (HET anhydride) and polyols based on trichlorobutylene oxide (27,57).

In general, ATH, halogens (chlorides and bromines) and phosphorus compounds are widely used commercially in flexible and rigid PUR foams (12,59). Flame retardants have been also used to obtain nonflammable foams using polymers different than PUR. Urea-Formaldehyde resins (60, 62) and brominated unsaturated polyester resins (61) are examples of this kind of approach. However these products are only combustion or ignition modified foams, having very different degrees of "built-in" fire retardance (11), but considering the good performance of some of these foams in
several tests (11) erroneous conclusions are usually made. As explained later on, the addition of flame retardants not only doesn't solve the problem but also can make foams considerably more dangerous in actual fires than the original foam.

In fact, in many cases (as early flame retarded PUR), the product although more difficult to ignite, can produce greater smoke and, in some cases, could even burn more rapidly than the standard PUR foam (1).

Generally a decrease in the flammability of an organic polymer decreases its fire damage but may not reduce (and even can dramatically increase) the deaths and injuries due to the production of smoke and toxic gases (63).

The problem with fire retardants is that at the high temperatures developed in a fire they may undergo pyrolysis giving combustion products, which are considerably more toxic (especially when bromine or chloride flame retardants are used) than those resulting, from the combustion of the "untreated" material (63).

Studies have showed (1,4,5) that in case of fire, flame retarded PUR can produce more smoke and, in some circumstances could burn faster than the standard PUR. In fact, fire retarded PUR can produce lots more HCN (4,5) and CO (5), producing more lab animal deaths (5,7) than the standard PUR. However other studies have showed that flame retardants do not significantly increase the production of toxic materials during the combustion of PUR (5). However, these different results only show that
both the polymer formulation and the type of fire retardant influence the toxicity of the materials and, therefore, must be carefully considered.

The nature of the gases produced during the combustion is really important considering that about 80% of the fire fatalities are caused by the inhalation of toxic gases (7).

2) Foaming of Nonflammable Polymers

The second approach to nonflammable foams consists in foaming known nonflammable polymers. This approach has not been extensively used, due to the difficulties in producing and processing the most known nonflammable polymers.

Consequently, in this case the research is not directed toward better nonflammability but toward retention of as much nonflammability as possible while having a processable polymer, useful for the industrial or in-place-foaming processes, which could be obtained by the introduction of some structural modifications to the polymer chain, such as (64):

- Introduction of flexibilizing units such as ether, sulfone or alkylene groups (which of course can reduce dramatically the nonflammability).
- Phenylation of the backbone.
- Use of fluorinated flexibilizing agents, which can drastically increase the cost.
In fact, the high cost (due to expensive raw materials as F, difficult or small scale production) of the most known nonflammable polymers is another serious limitation to this kind of approach.

Different polymers have been reported as fire resistant. There are several sources (17, 65, 66, 67, 68, 69, 70, 71) which compare the fire resistance (based on LOI or other parameters) of the most common fire resistant polymers. LOI (ASTM D-2863) is defined as "the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that will just support flaming combustion of a material initially at room temperature under the conditions of this test method" (72).

The minimum value of LOI for which a polymer is considered as fire resistant is 22 (the typical oxygen content in air), however higher minimum values as 26 (65) and 30 are arbitrarily fixed by different authors. However these values are too small and polymers with LOI close to them would require several other tests for applications requiring fire resistance. In fact, as stated in the LOI ASTM method (72), the value of LOI has no implications about burning characteristics of polymers under actual conditions. In table II-2 are summarized some of the above mentioned reviews about fire resistant polymers.

In spite of the long list of fire-resistant polymers given in table II-2, there are only a few reported fire-resistant foams (excluding those flame retarded, previously mentioned). As mentioned before, this is mainly due to the difficult processability of most of the fire-resistant and/or thermally stable polymers (normally processed by injection mold: polyesther
TABLE II-2. FIRE RESISTANCE OF SOME PLASTICS

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>LOI</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate</td>
<td>27</td>
<td>65,71,79</td>
</tr>
<tr>
<td>Nomex R</td>
<td>28.5</td>
<td>65</td>
</tr>
<tr>
<td>Polyphenylene oxide</td>
<td>29</td>
<td>71</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>30-32</td>
<td>17,65,70</td>
</tr>
<tr>
<td>Polyphenylene terephthalate</td>
<td>31-33</td>
<td>66</td>
</tr>
<tr>
<td>Polyamide 6.6</td>
<td>32</td>
<td>66</td>
</tr>
<tr>
<td>NORYL R SE-100 (Polyphenylene Oxide, FR)</td>
<td>33</td>
<td>17,70</td>
</tr>
<tr>
<td>Polyetherether Ketone (PEEK)</td>
<td>24-35</td>
<td>17,67,70</td>
</tr>
<tr>
<td>Polyether Polyurethane</td>
<td>33</td>
<td>74</td>
</tr>
<tr>
<td>Polyarylates (Aryler R or Ardel R)</td>
<td>34</td>
<td>17,70,79</td>
</tr>
<tr>
<td>Polyethersulfone (PES) (VICTREX R)</td>
<td>34-42</td>
<td>17,68,70</td>
</tr>
<tr>
<td>Phenol-Formaldehyde Resin</td>
<td>35</td>
<td>65</td>
</tr>
<tr>
<td>LEXAN R/920 (Polycarbonate, FR)</td>
<td>35</td>
<td>17.70</td>
</tr>
<tr>
<td>Polyarylsulfone</td>
<td>36</td>
<td>66</td>
</tr>
<tr>
<td>Liquid Crystal Polymcr (VECTRA R)</td>
<td>37</td>
<td>80</td>
</tr>
<tr>
<td>Polyaryl Ether Ketone</td>
<td>35-45</td>
<td>66,67</td>
</tr>
<tr>
<td>Polyarylate (DUREL R)</td>
<td>38</td>
<td>81</td>
</tr>
<tr>
<td>Polyimide foams (Solimide R)</td>
<td>38-43</td>
<td>82</td>
</tr>
<tr>
<td>Polyether Ketone Ketone (PEKK)</td>
<td>40</td>
<td>17,70</td>
</tr>
<tr>
<td>Polyamide-Imide</td>
<td>43</td>
<td>79</td>
</tr>
<tr>
<td>Polyphenylene sulfide (PPS, no additives)</td>
<td>44</td>
<td>73</td>
</tr>
<tr>
<td>Poly(Vinylidene Fluoride)</td>
<td>44</td>
<td>65</td>
</tr>
<tr>
<td>Phenolic foams (KOOLPHEN R K)</td>
<td>45</td>
<td>83</td>
</tr>
<tr>
<td>Polyetherimide</td>
<td>48</td>
<td>66</td>
</tr>
<tr>
<td>Polyphenylene sulfide</td>
<td>48</td>
<td>66</td>
</tr>
<tr>
<td>Polybenzimidazole</td>
<td>41-48</td>
<td>65,77,79</td>
</tr>
<tr>
<td>Polyimide (Pyromellitimidie)</td>
<td>50</td>
<td>79</td>
</tr>
<tr>
<td>Fluoropolymer Resin (HALAR R)</td>
<td>52-60</td>
<td>84</td>
</tr>
<tr>
<td>Polyvinylidene Chloride</td>
<td>60</td>
<td>65,71,85</td>
</tr>
<tr>
<td>Poly-tetrafluoroethylene</td>
<td>95</td>
<td>16,65,71,79</td>
</tr>
<tr>
<td>Polyfluoralkoxy resin (PFA)</td>
<td>&gt;95</td>
<td>85</td>
</tr>
<tr>
<td>Fluorinated ethylene-propylene copolymer (FEP)</td>
<td>&gt;95</td>
<td>8.5</td>
</tr>
<tr>
<td>Polychlorotrifluoroethylene (PCTFE)</td>
<td>100</td>
<td>8.5</td>
</tr>
</tbody>
</table>
polyurethane (74), polyphenylene sulfide (73), PEEK (67), polyethersulfone (68), PAEK (14), polyamide-imide (14), polyphenylene sulfide (65), polyarylsulfone (14) or extrusion: polyester polyurethane (74), PEEK (67), PAEK (14), polyethersulfone (68), polyarylsulfone (14)), and to the relatively high costs of most of the fire-resistant and/or thermally stable polymers (some examples are polyetherimide: 10 US $/lb (66), polyethersulfone: 13 US$/lb (66), polyaryletherketone: 40 US$/lb (66), polyamide-imide: 19-20 US$/lb (14)).

3) New Polymer Systems

The third approach, which corresponds to this research, consists in developing new polymer systems with the required characteristics (nonflammability, ease of foaming, flexibility, etc.). Of course the development of new polymers has an inherent difficulty (requires more creativity, time and money) which makes this route a lightly traveled one. With the possible exception of certain specialty polyimide foams (such as those containing furfuryl alcohol) we have not found in the literature any polymer systems, specifically developed for nonflammable foams.

B- Thermal Stability

Nonflammability and thermal stability are different characteristics of the polymers. Some polymers are nonflammable but not thermally stable and vice versa. Flame retarded nonthermally stable polymers (e.g. flame
retarded PUR) decompose under fire or heating, generating smoke and toxic gases, since the flame retardant additives cannot protect the polymer backbone against thermal degradation. As stated by Pearce (75): "Polymers which can be largely degraded at relatively low temperature" ... to give "monomer, dimer or other low molecular weight combustible volatiles" give "low oxygen index values" (LOI). In general, the conditions for inherently good nonflammability are (75) thermal stability (it means the polymer degrades only at high temperature) and nonflammability of the decomposition products.

In this work not only inherently nonflammability but also thermal stability are required in order to get "truly" fire-resistant foams useful and safe for exigent applications.

In general, the thermal stability of polymers can be achieved in several ways, as follows:

a) Use of strong chemical bonds (tables of bond strength values are available in the literature),

b) Use resonance stabilization (because more energy would be needed for bond rupture).

c) Try to get polybonding, forming "ladder" polymers, so the chains cannot be broken by the rupture of only one bond.

These are the classical conditions for thermal stability of polymers. They tend to produce insoluble and/or infusible polymers. However, in the formulation of a polymer, its processability can become more important.
than its thermal stability. For this case, in which easily foamable polymers are required this aspect becomes even more important.

A classification of polymers in ascending order of their thermal stability can be made, as follows (64,76,77,78):

a) Aromatic polymers (with or without functional groups).
b) Aromatic polymers with heterocyclic groups.
c) Ladder polymers.
d) Inorganic (or partially inorganic) polymers.

C- Polyimide Foams

The only current, commercial foams that are inherently nonflammable and thermally stable are the polyimide foams. The first polyimide foams, generically called SKYBOND® and designated as RI-7271-01, RI-7271-06, RU-7271-12, and RI-7271-18 (77) were introduced by MONSANTO in 1970 (86); the numbers 01, 06, 12 and 18 indicate the approximate density in lb/ft³ (77). In 1978 Upjohn introduced its polyimide 2080® foam, and in 1980 the LMB 1907® foam was introduced by CIBA-GEIGY (86). By this time ICI produced a lightweight syntactic foam consisting on a mixture of polyimide (QX-13 Resin) and silica microballoons (77).

The well-known Solimide® foam was introduced in 1981, by the Solar Division of International Harvester, which had been developed under NASA contracts (86). This product is reported to be fire-resistant, lightweight, flexible and resilient over a wide temperature range, and emits
virtually no smoke or incapacitating toxic by-product when exposed to
open flame (82). It has found applications in the aircraft (private,
commercial and military) and in the marine (82,86). This material was
used in insulation aboard the Space Shuttle Columbia (85). Commerically
several grades of SolimideR (from Imi-Tech) are available, being some of
them the SolimideR TA-301 (with LOI 38 or 43) (82) and SolimideR AC-
406 (with LOI 38) (82).

Chemically the most common types of polyimide foams are copolyimides
and terpolyimides. The copolyimide foams are derived from:

a) "A diester of 3,3', 4,4'-benzophenonetetracarboxylic acid, and an
aromatic diamine and a heterocyclic diamine" (88),
b) "An alkyldeister of 3,3', 4,4'-benzophenonetetracarboxylic acid and at
least two aromatic diamines which are free of aromatic moieties" (89),
c) A half ester of the 3,3', 4,4'-benzophenonetetracarboxylic acid reacted
with one or more primary diamines to form an essentially monomeric
precursor (90,91),
d) A diester of 3,3', 4,4'-benzophenonetetracarboxylic acid with 3,3' and
4,4'- benzophenonetetracarboxylic acid mixed with a meta- or para-
substituted aromatic diamine, an aliphatic diamine and a solid blowing
agent (92).

An example of this type of reaction is (93):
The terpolyimides are "prepared from tetracarboxylic acid esters and combinations of heterocyclic, aromatic, and aliphatic diamines and artifacts composed of those terpolymers" (94).

There are several other polyimide foam formulations, some of which include other compounds such as oxoimides (95), oximes (96), oximines (97) or metallic catalysts such as Cu, Cr, K, Co, Li, Ca, Cd, Ba, etc. salts (98).

One of the most serious drawbacks of these polyimide foams is that they cannot be foamed in place. However, an ambient cure polyimide foam has also been reported (99). In this case, an aromatic dianhydride (e.g. pyromellitic anhydride) is polymerized with an aromatic polyisocyanate (e.g. polymethylene polyphenyl isocyanate, PAPI) in the presence of an
inorganic acid (e.g. dilute sulfuric, phosphoric, hydrochloric or nitric acid) and furfuryl alcohol (99). The exothermic reaction between the alcohol and the acid provides the heat required for the polymerization of the other reactants (99). The main problem with this particular type of polyimide foams is that its polymerization is difficult to control and for that reason this process is not commercially used.

In general, the main drawbacks of the polyimide foams are: high cost, poor resiliency, and not easily foamed-in-place.

D- Polybenzimidazole (PBI) Foams

Polybenzimidazoles are well-known high-temperature resistant polymers (64,77,100). They contain the following benzimidazole units in their backbone (86):

The PBI foams were introduced in 1968 by Narmco, under the commercial names Imidite SA and PC, which are syntactic poly (m-phenylenebenzimidazole) foams (64,77,86). The syntactic foams are produced from blends of the prepolymer and fibrous fillers (carbon or PBI), or silica or phenolic microspheres (77). Low density PBI foams with good thermophysical properties has been produced reacting 3,3'-diaminobenzidine, containing 95% of ortho-diamine groups, with diphenyl isophthalate (100). The foam is formed between 185 and 275 °C (77,100) but then has to be heated (at a rate of 2 °C/min.) to be cured between 465
and 525 °C (64,77,100). Phenol is produced during the formation of the benzimidazole ring (100).

Using the appropriate molds these foams can be produced in the desired shapes (77) which added to the good fire resistance (LOI about 48 (77) and high char yield of about 76% at 800 °C (64)) are the main advantages of this kind of foams (64,77).
The main drawbacks of these PBI foams are: high cost, low strength and not useful for foaming-in-place.

E- Polyphosphazene Foams

Polyphosphazenes are polymeric materials which exhibit excellent flammability properties (72). In fact, LOI of polyphosphazenes have been reported in the range 27-67 (101). As discussed later on, their general formula is (72):

\[
\begin{array}{c}
\text{R} \\
\text{N=\text{P}} \\
\text{R}
\end{array}
\]

and they can be open-chain or cyclic polyphosphazenes (101).

In most cases the chemical reactivity and, especially, the hydrolytic instability have limited the application of the polyphosphazenes. Several polyphosphazenes have been reported as hydrolytically instable being the
polyhalophosphazenes (case in which \( R_1 \) or \( R_2 \) are Cl, F or Br) especially affected by this phenomena.

However, completely substituted poly(organo)-phosphazenes (it means \( R_1 \) and \( R_2 \) are organic groups) are normally stable to atmospheric moisture but most of them are still affected by bases or acids (101,102).

Several polyphosphazene foams have been reported. One of them (72) corresponds to the case in which \( R_1 \) and \( R_2 \) are phenoxy or substituted phenoxy groups. These polymers are commercially available from Ethyl Corporation as EYPEL™ A and chemically are Aryloxypolyphosphazenes (72). LOI as high as 46 have been reported for these flexible foams.

Other polyphosphazene foams have been patented; some of them have been reported as flameproof (103) and fire-retarded (104) but in other cases (105,106,107,108) nothing is mentioned about this property. However, due to their relatively high P, N and halogen contents presumably are at least fire-retardant foams.

The polyphosphazene foams are not widely used, especially due to the possibility of hydrolytic decomposition and their poor physical properties. Another important drawback is that the combustion of these foams evolve toxic gases, including HCN, CO, and \( \text{NO}_2 \) (85).
F- Other Foams

Many other foams have been reported in the literature as nonflammable or fire-retardant; however, generally no data about their LOI or other flammability parameters are available. Some of the most known foams of this type are:

1) Polysiloxanes: this type of polymers, also known as siloxanes or polyorganosiloxanes (or in some cases silicone foams) have had commercial success as sealants, encapsulants, and elastomers (64). Polysiloxanes are characterized by the group SiOSi. Its general formula is (79):

\[
\begin{array}{c}
R \\
\mid \\
\text{Si—O—} \\
\mid \\
R
\end{array}
\]

and commonly in its production as foams Pt is used as catalyst (109,110,111,112,113). Some of these foams have been reported to have good flame resistance (109,110,111), sometimes achieved with flame retardants as aluminum hydroxide. They also have good thermal stability (109,111) up to 1500 °C (109). Also there is a patent (114) for an organosiloxane system which can be foamed in place; however, nothing is mentioned about the flammability of the product.
2) POLYSTYRENE FOAMS: In general, polystyrene is a flammable material (LOI: 17 (77)) which can be easily foamed (115). However, using flame retardants (the same kind of approach considered before for PUR foams) flame-retardant polystyrene foams can be obtained (115,116,117). The flame retardants used in this case are: a compound known as BAP, chemically 2,2-Bis(4-aloxy-3,5-dibromophenyl) propane (116), or a mixture of antimony oxide, zinc borate, alumina hydrate and an halogenated hydrocarbon (117) or halogenated (brominated or chlorinated) compounds (115).

3) PHENOLIC FOAMS: Phenolic or phenol-formaldehyde resins are one of the oldest and most studied polymeric systems. Several formulations for reducing the flammability of this material have been reported (13), as follows: use of methyl-1,1,2,2-tetrafluoro-ethylmethylphosphine oxide, or 4,4'-dioxidyphenyl-sulfone, or 4,4'-diphenylphenylphosphine oxide during the condensation; or use of compounds which react with the formaldehyde as urea, melamine, dicyandiamide or triazine compounds; or chlorination or bromination of the resin; or use of fillers such as asbestos, glass fiber, perlite, etc; or use of the known flame retardants such as ATH, zinc oxide, orthophosphoric acid, organophosphates, phosphonates, etc. With these materials, different grades of flame retardance have been achieved for the phenolic resins and the phenolic foams.

Some other modifications have been patented for producing fire-resistant phenolic foams (60,62,118), involving compounds as phosphoric esters (118), resorcinol and furfural (60), furane resin and furfuryl alcohol (62). However, these materials are rigid (useful as insulation and building
materials), as expected when phenolic resins are used. Another important drawback of these foams is the evolution of formaldehyde and some lethal combustion gases (especially CO) during fires (85). KOOLPHENR K, a phenolic foam with LOI 45, is commercially available for insulation applications (83).

4) POLY(CARBODIIMIDE) FOAMS: Poly(carbodiimides) are polymers with relatively good thermal stability (119). Some foams have been prepared with this material by catalytic condensation of two isocyanate moieties (119) which liberates carbon dioxide useful as foaming agent. The most common catalysts are cyclic phosphorous compounds (119), such as oxides of phospholenes and phospholanes (119) as well as phosphorus-nitrogen heterocycles. However, these foams exhibit values of LOI of only about 29 (119) which make them unsuitable for many applications.

5) EPOXY-BOROZINE FOAMS: Some self-extinguishing foams, consisting of an epoxy resin, a primary polyamine (e.g., p,p'-diaminodiphenylsulphone) and a trialkoxyboroxine (e.g., trimethoxyboroxine) have been reported (115). The trimethoxyboroxine reacts with the amine to form a crosslinked polymer containing B-N bonds, and liberates 3 moles of methanol per mole of boroxine. The reaction is exothermic and no foaming agent is required. The foams are self-extinguishing because under fire B₂O₃ is deposited on the surface, thus smothering the fire (115).

6) FLUOROPOLYMER FOAMS: In general most tractable (i.e. fusible or soluble) polymers can be foamed using heat and blowing agents. So,
considering the existence of fluoropolymers with excellent LOI (see Table II-2) this seems to be a good possible source for nonflammable foams. In fact, some perfluoropolymers have been foamed for medical applications (120) and a fluoropolymer resin (HALAR® from Ausimont) has been also foamed for wire coating (84). However, these fluoropolymers when heated (in the presence or absence of flame) produce strong acids (84) including HF (if both hydrogen and fluorine are present in the molecule) (85), carbonyl fluoride, perfluoroacetic acid, and perfluoroisobutylene (85,120) which is a extremely toxic gas (121). The other disadvantage of these foams would be their high cost, typical of F-containing compounds.

7) OTHER FLAME RETARDED FOAMS: Several other common polymeric materials have been flame-retarded and foamed, as follows:
- PVC flame retarded with zinc borate and a synergic mixture of copper cyanate and Sb₂O₃ (122).
- Polychloroprene (neoprene) flame retarded with ATH (123).
- Brominated unsaturated polyester resins, in which the Br provides the flame retardance (61).

G- Concluding Remarks

Extensive examination of the literature has confirmed that none of the existing foam systems (some of which are very expensive materials) meet all the requirements for an inherently nonflammable, thermally stable foam system, capable of foam-in-place production. The best systems are polyimides, polybenzimidazoles and polyphosphazene foams. Polyimide
foams are nonflammable but expensive, and cannot be foamed-in-place. Polybenzimidazole foams have the same drawbacks. Polyphosphazene foams don't exhibit good resiliency, may show hydrolytic decomposition and their combustion products are toxic gases.

For the previous reasons, we have concentrated in this research on developing completely new chemical compositions.
III- LITERATURE REVIEW: COMBUSTION TOXICOLOGY

An important aspect in the study of fire resistant polymers is the health effect of the combustion products and the heat produced by the burning material.

A large number of products are generated from the combustion of polymeric materials. Depending on the composition of the material, the most common products are (124): Carbon monoxide, carbon dioxide, nitrogen oxides, halogen acids, hydrogen cyanides, particulate aerosols and some complex organic (or in some cases inorganic) moieties liberated during the thermal degradation of the material.

Of course, the most common deadly gas generated in the combustion of the common polymeric materials (especially polymeric foams) is CO (because most the used polymers are organic compounds). Other common gases are HCl, HCN, SO₂ and phosgene (85) but also NO, NO₂, NH₃, H₂S, COS, HF, HBr, benzene, phenols, aldehydes,... can be found.

Paradoxically, some of these gases (considerably more toxic than CO) are generated by compounds introduced to the polymeric material as flame retardants.

The toxic actions that make these materials life or health-threatening factors in fires are as follows (124):
1) **CARBON MONOXIDE**: this is the dominant factor in causing death in fires (124), responsible for 70 to 80% of the human deaths in fires (124). The reason for this is that most of the materials used in construction and furniture (including polymeric materials, wood, etc) are organic compounds which generate CO by incomplete combustion. Since PUR foams are so extensively used in household furniture the amounts of CO generated during the combustion of PUR are especially interesting. Results of different fire tests for rigid PUR foam are as follows (125):

- **Nordtest NT - Fire 004**: 71 mg CO / g PUR burnt

- **DIN 53436 Test Method**: 158 mg CO/ g PUR burnt

- **Cone calorimeter**: 220 mg CO/ g PUR burnt

---

*NT-004 test method studies burning behaviour, temperature increase, and smoke emission. The equipment consists of a box 20cmx20cm on four of the six walls in which is placed the tested polymer (usually lining material). Air inlet and exhaust chimney are mounted on the back side wall. A gasburner is mounted on the floor plate having an energy output of 5 KW at 3.2 l/min. of propane (125).  

**Core Calorimeter**: there are several versions of this equipment. This particular version takes samples of size 20 cmx20 cm mounted in a horizontal position on top of a load cell. Above the sample there is a cone heater and a spark ignitor. Gas samples are taken in fan ventilated exhaust duct mounted above the cone heater. The radiation used has been 50 KW/m² and there is free convection ventilation over the sample. The ventilation rate in the fume hood and ventilation duct is about 5 lt air/sec (125). 

*** The equipment for the DIN-53436 test (Moving Tube Furnace) consists of a quartz tube, 100 cm long and 40 mm outer diameter. A round moving furnace is placed around the quartz tube. The furnace gives temperatures inside the tube of at least 600 °C. A tray 40 cm long holds the samples and a reference body which controls the inside temperature. The furnace is moved at a specified speed over the sample heating continuously new sections of the material during the experiment. The fumes from the material may be ignited with a igniter if necessary (125,126).
The CO when inhaled is transported across the lung membranes into the blood stream. It combines (reversibly) with the hemoglobin to form carboxyhemoglobin (124). The problem is that hemoglobin has an affinity for CO about 200 times bigger than for oxygen (127). Carboxyhemoglobin produces neuromuscular incapacitation reducing the individual's capacity to escape from fire. Even low concentrations of CO causes drastic reductions of the judgment capacity and visual acuity (127). Table III-1 (124) shows the effects of different CO concentrations in humans.

So, in conclusion, the CO is highly dangerous in a fire not only because relatively high levels produce death but because it reduces the escape capability forcing the individual to inhale higher quantities of CO and the rest of the dangerous generated gases.

2. HYDROGEN CYANIDE: HCN is considerably more toxic than CO. However, hydrogen cyanide alone is not as frequent a cause of death as CO (128). Concentrations between 300 and 350 ppm of HCN can cause death within 10 minutes (124). HCN is a fire hazard when nitrogen-containing polymers (PUR, polymethanes, polyamides, polyacrilonitriles, etc) (124,128) are present. In fact, the production of HCN during fire is one of the biggest problems of PUR foams, and must be carefully considered when used flame retarded PUR. Studies for rigid PUR foams show values of about 5.2 mg HCN by g of material burnt in a DIN 53436 test (125).

The HCN reacts with the trivalent iron of cytochrome oxidase in the body's cells and inhibits the cellular oxygen exchange causing death. It has been estimated that a concentration of about 1 mg/Lt of HCN in the blood is
<table>
<thead>
<tr>
<th>CO (ppm) x Time</th>
<th>Blood Level of Carboxyhemoglobin (%)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 x 90 min.</td>
<td>0-1</td>
<td>No effects</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>Impaired time interval discrimination</td>
</tr>
<tr>
<td>100 x 50 min.</td>
<td>3.0</td>
<td>Changes in visual acuity</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>Impaired performance in psychomotor tests and in visual discrimination</td>
</tr>
<tr>
<td>200 x 4 hrs.</td>
<td>24.8</td>
<td>Mild headache, changes in evoked response in encephalogram</td>
</tr>
<tr>
<td>500 x 2 hrs.</td>
<td>25.4</td>
<td>Increased severity of preceding changes</td>
</tr>
<tr>
<td>1000 x 2.5 hrs.</td>
<td>31.8</td>
<td>Severe headache, decline in performance of manual dexterity tests. Increasing change in visual evoked response. Fatigue of hands and fingers.</td>
</tr>
<tr>
<td>1500-2000 x 1 hr.</td>
<td>35</td>
<td>Dangerous to continuation of neurological and decision-making functions</td>
</tr>
<tr>
<td>4000 x 1 hr.</td>
<td>50</td>
<td>Fatal</td>
</tr>
</tbody>
</table>
lethal (128), but the exact value is difficult to be established because the
detection of the cause of death during a fire is difficult and also because
the analysis HCN in blood is difficult (124). Besides that, HCN can either
appear or disappear from the blood of autopsied victims (124).

According to studies (127) 270 ppm (or higher) of HCN in air are
immediately fatal to humans. 180 ppm are fatal after 10 minutes. 135
ppm are fatal after 30 minutes and 110 ppm after 1 hour.

Another aspect to consider is the additive (synergistic) effect of HCN an
CO, detected in several studies (124).

3) NITROGEN DIOXIDE: Nitrogen dioxide (NO₂) is highly toxic and
can adversely affect the human body if inhaled or if it comes in contact
with skin or eyes (127). Exposure can produce severe breathing
difficulties which can cause death.

The effects expected in humans from exposure to NO₂ for one hour are
(127): 25 ppm produce chest pain and respiratory irritation; 50 ppm
produce pulmonary edema with possible subacute or chronic lesions in the
lungs; 100 ppm cause pulmonary edema and death.

Nitrogen dioxide is generated in the combustion of several nitrogen-
containing polymers. For the case of rigid PUR foam several values have
been reported (125) as follows:

- 4.8 mg NO₂/g PUR in Nordtest NT- Fire 004
- 6 mg NO₂/g PUR from the cone calorimeter
4) PARTICULATE MATTER: Most of the research on the toxicity associated with fires (and for this case, with polymer burning) has focused on vapors and gases. However, the smoke produced by the burning of polymers also contains particulate components (129). The physiological effects of these products on the human beings are determined by the physical and chemical characteristics of the particles (124,129). The main physical characteristic is the size of the particle, because it determines the site of deposition in the respiratory tract (124,129). Particles greater than 10 μm (aerodynamic diameter) are not considered breathable. Particles in the 5-10 μm range are collected on the surface of the nasopharynx (129). Particles in the range 1-5 μm deposit on the surfaces of the tracheal-bronchial area (124). Particles with diameter lower than 1 μm reach the alveoli and are deposited in the lungs (124).

Toxic substances exert different toxic effects according to the point of deposition, being the lungs the organs with the strongest toxicological effect (129). The retention of particles in the lungs depends partially on their solubility in the milieu of the lung (129).

It is especially important, for this case, to consider the effect of particles of flame retardants (or thermal degradation products of flame retardants). A general rule is that water soluble salts (as most chlorides) will clear the lung rapidly while insoluble products (as metallic oxides) will be retained for periods as long as hundreds of days (129). As mentioned before, organobromine and organochlorine compounds are widely used with Sb₂O₃ as flame retardants for PUR (16,17,28). However, when most of these products are heated above 250 °C they produce HBr or HCl (71) which
then react with the antimony oxide/polymer substrata to generate volatile antimony halide and oxyhalides (71), compounds dangerous for human health.

According to this information it is very important to consider the toxicological aspects involved in the selection of foams for nonflammable applications. However, this factor seems to be commonly forgotten. For the specific case of aircraft seat cushions there is an FAA (Federal Aviation Administration) regulation (issued in 1984 and effective since November 1987), based on a "two-minute test in which a seat mock-up is exposed to a large burner that simulates the heat output of a jet fuel fire" (120). The regulation establishes that "no more than 10% of the cushions' weight may be consumed, and there must be no flame spread across any surface of the seat" (120). These requirements are relatively rigid and basically are achieved using fire-blocking covers (based on PBI, or PBI/aramid blends) for the PUR foams (130) or using specially treated (flame retarded) PUR foams. However, the FAA regulations do not include anything (120) about perhaps the most important factor: the emission of toxic gases during an aircraft cabin fire. Some aircraft companies have internal standards or guidelines regarding toxic emissions (120) but, of course, this is not enough. Something similar occurs with upholstered furniture: there are regulations regarding heat release* and cigarette ignition** (131) but not about toxic gases production during combustion.

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* Standard Fire Prevention Code, 4302.1: "Any item of upholstered furniture, mattress or wardrobe shall produce a maximum instantaneous net peak of heat release of 500 KW or less" (131).
** Standard Fire Prevention Code, 4302.2: "Upholstered furniture shall resist ignition by cigarettes..." (131).
IV- SCOPE OF THIS RESEARCH PROJECT

In view of the serious limitations of the currently available polymer foams we set out to generate novel foam systems with inherent nonflammability and thermal stability by synthesizing polymer networks based largely on elements other than carbon and hydrogen. This approach was conceived and initially reduced to practice by Dr. C.D. Armeniades and Mr. G. Nichols, who have denoted it with the term "alternative foam chemistry". The generation of alternative chemistry foams comprises two consecutive processes:

a) Synthesis of the foam system components: these are liquids or low-melting solids, which remain stable when stored at ambient temperatures, but can react rapidly when properly mixed and/or heated; and

b) Foam-in-place procedures: the mixing and/or heating of the foam system components in the proper combinations and proportions, whereupon they react rapidly to polymerize with the concurrent evolution of gaseous byproducts, which serve to expand the nascent polymer network, thereby generating rigid or flexible foams.
V. MATERIALS AND METHODS

A. Chemical Building Blocks

A large number of different reagents were investigated in these experiments. Nitrogen-containing reagents include urea, melamine, ethanolamine (MEA), diethanolamine (DEA), hydrazine, caprolactam, ethylurea, cyanuric acid, triethylenetetramine (TETA), etc. Phosphorus compounds include: phosphoric acid (H₃PO₄), P₂O₅, trimethyl phosphate, etc. Various other elements and compounds such as Al (ATH, metallic Al), V (V₂O₅), Sb (Sb₂O₃), B (H₃BO₃), etc. were used in these experiments. In the end, four materials due to their properties and effectiveness in our foamed polymer synthesis emerged as the most used chemical building blocks. These materials are phosphoric acid, trimethyl phosphate, Hexakis Methoxy Methylene Melamine and trihydroxyethyl-isocyanurate (THEIC). These are all (relatively) inexpensive industrial chemicals, hence they provide a sound practical basis to the new foam systems.

1) H₃PO₄: is known as phosphoric acid, orthophosphoric acid or white phosphoric acid (132). Commercially used in aqueous solutions (85%). The material is viscous, colorless, odorless, and miscible with water (132). It is a strong acid, corrosive, and moderately toxic by ingestion and skin contact (132). It is a corrosive irritant to skin, eyes and mucous membranes (132). Its functionality is 3 and its advantages in this research are based on its high content of pentavalent P (31.6%), low cost, and good reactivity.
2) Trimethyl phosphate (will be symbolized as TMPO₄), its chemical structure is:

\[
\text{O}\\
\text{H}_3\text{C-O-}\text{P-O-CH}_3\\
\text{CH}_3
\]

This material is liquid (m.p.: -46 °C), with b.p.: 197 °C, d: 1.197 (133), its a toxic liquid, cancer suspect agent (133), mutagen (133), and irritant.

Its functionality is 3 and its advantages for this research are due to its high pentavalent P content (22.1%), low cost, stability in storage and relatively good reactivity.

3) Hexakis Methoxy Methylene Melamine: this product is commercially available from Cyanamid as CYMEL®-301 (134) and is a modified melamine-formaldehyde resin. The commercial product is a mixture (134) containing the hexakis methoxy-methylene melamine (an s-triazine), which formula is:

\[
\text{CH}_3\text{O-CH}_2\text{N-}[\text{C-N-C-CH}_3\text{OCH}_3]_6\text{N-N-C-CH}_3\text{OCH}_3\\
\text{CH}_3\text{O-CH}_2\text{N-}[\text{C-N-C-CH}_3\text{OCH}_3]_6\text{N-N-C-CH}_3\text{OCH}_3
\]
This triazine is nontoxic but the resin becomes harmful due to the content of formaldehyde (typically <0.3%) which can cause skin irritation and has caused cancer in laboratory animal tests (134,135). The resin is a clear viscous liquid, with specific gravity of 1.2 and volatiles lower than 2% (in volume) (134). Its applicability in this research is based on its high content of good quality N (21.5% calculated according to the described formula), its stability, its moderate cost, its relatively good reactivity with different functional groups (esters, alcohols, amides, carboxylic acids, etc.), and its functionality (f=6) which allows the product to crosslink easily.

4) Trihydroxyethylisocyanurate (THEIC): also called 1,3,5-tris (2-hydroxyethyl) cyanuric acid or even 1,3,5-tris (2-hydroxyethyl)-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione. This material is solid (m.p.: 136-140 °C (133)), and irritant. Its chemical formula is:

![Chemical structure of THEIC](image)

Commercially available from BASF. The advantages of this material are high content of good quality N (16.1%), stability and nontoxicity, moderate cost, and relatively good reactivity with different functional groups. Its functionality is 3.
5) AZODICARBONAMIDE: this compound was extensively used in this research as a foaming agent, for which about 1-2% of this compound was included in several formulations.

Azodicarbonamide, also known as azobisformamide, and commercially available (pure or activated) with many different names (Celogen from UNIROYAL (136), FICEL from Schering Berling (137), etc.) is one of the most important solid blowing agents in the plastic industry (EAB). Its formula is:

\[
\begin{align*}
\text{H}_2\text{N} \equiv \text{N} \equiv \text{N} \equiv \text{N} \equiv \text{H}
\end{align*}
\]

and normally is produced by reacting hydrazine with urea to produce hydrozodicarbonamide which is subsequently oxidized to azodicarbonamide (115). It has yellow color, and normally gives yellow color to the foams. It decomposes producing gas at temperatures between 175 and 216 °C (115) but can be activated (with zinc oxide, zinc stearate, dibasic lead phosphite, etc. (136)) for decomposing at lower temperatures, or it also can react, generating gases, with some functional groups of the polymer.

The gases produced are a mixture (115,136) of nitrogen (65%), CO (31.5%) and small quantities of ammonia and CO\(_2\) and other gases. The decomposition residues are white, odorless, and nonstaining (115).

The decomposition reactions are as follows (136):
The reaction generates about 220 cm³ of gas @ STP for each g. of reacted azodicarbonamide (136).  
The advantage of this product over many other different solid foaming agents (like diazaminobenzene, azobis(isobutyronitrile), N,N'-Dinitrosopentamethylenetetramine (115), p-toluene sulfonyl hydrazide, p-toluene sulfonyl semicarbazide, p,p'-oxybis benzene sulfonyl hydrazide (136)) is that azodicarbonamide does not support combustion and is self-extinguishing (115).

As much of the chemical products azodicarbonamide must be carefully handled. Contact with eyes may cause irritation, and repeated minimal inhalation exposure can cause respiratory sensitization and occupational asthma (136). The oral toxicity, LD₅₀ (rats), is 6.8 g/Kg (136).

B. Apparatus and Foam-in-Place Procedure

Most of the reactions involved in the synthesis of the foam system components were carried out using ordinary bench chemistry
equipment: heater-stirrer plates, glass reaction flasks, condensers, collectors, etc.

Foam-in-place procedures at controlled temperatures were carried out in constant-temperature baths, containing heat-transfer salt (HTS).

The heat-transfer salt (HTS) is an inorganic salt mixture consisting of potassium nitrate (53%), sodium nitrate (40%), and sodium nitrate (7%) (138).

The mixture melts at 142 °C (138, 139), but its melting point can be reduced by water addition (139).

The main advantages of this bath for this research are: it is nontoxic and chemically stable, and has a sufficiently high melting point which permits relatively good control of the temperature during the foaming process. Especially useful is its negligible vapor pressure (139), so no vapors (which could be re-condensed on the foam surface) are generated by this salt mixture. The HTS bath also allows excellent visual and observation control of the foaming process which cannot be obtained in an oven. Consequently, it was used in preference to the constant-temperature oven.

The HTS system provides homogeneous heating to the bottom and the sides of the container in which the foam is formed; however, the top is not well heated by this method, so heating of the top surface of the foam with a hot-air gun or completion of the foam cure in the oven are required for some formulations.
VI- DESCRIPTION OF SELECTED FOAM SYSTEMS

About 2,000 foam formulations were prepared and examined in the course of this work. Of these systems about 166 were considered nonflammable by our simple (but surprisingly effective) test: ignition by an ordinary butane lighter*. In the following Sections we describe the preparation and properties of seven of the nonflammable formulations, which on the basis of their overall properties (in our opinion) represent foam systems worthy of further consideration and development.

A- Foam BL-1

1) Ingredients

a) Solution XIII : 1 mole THEIC (trihydroxyethyl isocyanurate)/
   3 mole TMPO₄ (trimethyl phosphate)

b) Solution VI : 2 mole CYMEL-301/1 mole Bisphenol A

c) Product 157 : 1 mole Terephthalic Acid
   2 mole H₃PO₄
   Some Epoxy (PET-810R CIBA-GEIGY)

2) Foam Component Preparation

* We have informally denoted this as the "BIC Flammability Test". When subjected to this test polyimide foams with LOI values of 39 will intermittently ignite with a tiny flame that self-extinguishes within a second or two. Polyimide foams with LOI of 43 will not ignite at all. We therefore assume that our formulations that past this test have LOI values in excess of 40. We consider these to be nonflammable formulations.
a) Solution XIII

Take: 1 mole THEIC (261 g)
3 mole TMPO₄ (420 g)

Mix and heat. At about 70 °C a clear product (solution) is obtained. Continue heating until reaching about 100 °C. Remove about 15-16% of the total initial weight.
The final product is transparent, lightly yellow, stable for months and has low viscosity (assumed MW= 575)

b) Solution VI

2 mole CYMEL (780 g)
1 mole Bisphenol A (228 g)

Start heating and mixing. At about 130 °C gets completely transparent (solution) and then (T about 160 °C) starts bubbling.
The heating must be stopped when the product starts changing from yellow to orange.
Quantitatively, about 5.4% of the initial material must be removed.
The final product is viscous, yellow, transparent, stable for months and no water soluble (Flasks can be cleaned by boiling diethyelene glycol).

c) Product 157

Mix: 1 mole Terephthalic Acid (166 g)
2 mole H₃PO₄ (230 g)
40 g Epoxy (PT-810 CIBA-GEIGY)
Mix and heat. Heat to about 70-80 °C and wait for bubbling. After high bubbling: stop heating. Only about 1-2% of the material is expected to be removed. The product is yellow, turbid, not highly viscous and it can separate in two phases after some time (typically 1-3 days). However, it is easily homogenized again by good mixing.

3) Foam-In-Place Procedure

In a small beaker (30 ml) mix:

- 5.6 g solution VI
- 4.2 g solution XIII
- 3.9 g Prod 157
- 0.1-0.2 g Azodicarbonamide (Foaming Agent)

Foam in HTS (Heat Transfer Salt) bath or in oven at T= 140 °C (takes about 2 min.).

The product is a yellow foam (of about 35 ml), nonflammable, flexible, stable for several days (at least 10).

4) Similar Foam Systems

Very similar foams can be produced without the foaming agent or replacing it by CaCO₃. In these cases the obtained foam is white but normally has lower volume (typically 30 ml) and takes longer to foam.

Other foams can be obtained by the following changes:

a) Replace solution VI by solution III (3 mole CYMEL/1 mole THEIC, mix and heat until about 120 °C and remove about 5.6% of the initial mass). In
this case the foam has similar characteristics but normally has higher densities.

b) Do not use the product 157 and use combinations of solution III and solution VI. Examples:
   5.2 g solution XIII
   3.5 or 4.0 g solution VI
   3.5 or 3.0 g solution III
   0.2 g Azodicarbonamide

   The foam is yellow, flexible, nonflammable, its volume is about 30-32 ml but it is not as stable as formulation described in part 3).

c) Do not use product 157 but use some Urea. Example:

   7 g solution III (If solution VI is used: Flammable)
   5.2 g solution XIII
   0.3 g Urea
   0.3 g Azodicarbonamide

   d) Use Azodicarbonamide (0.4 g) and Al (0.4 g) for still better volume and silver color (Foaming time about 31/2 min.).

4) Several other foams have been produced including solution VI, solution III or solution XIII but are out of the scope of this report.
B- Foam 510

1) Ingredients

a) Solution XIII  
b) Solution VI  
c) Product 477  

2) Foam Component Preparation

a) Solution XIII

Take: 1 mole THEIC (Trihydroxyethyl isocyanurate) 261 g  
3 mole TMPO₄ (Trimethyl phosphate) 420 g  
Mix and heat. At about 70 °C a clear product (solution) is obtained. Continue heating until reaching about 100 °C. Remove about 15-16% of the total initial weight.  
The final product is transparent, lightly yellow, stable for months and has low viscosity (assumed MW= 575)

b) Solution VI

2 mole CYMEL (780 g)  
1 mole Bisphenol A (228 g)  
Start heating and mixing. At about 130 °C gets completely transparent (solution) and then (T about 160 °C) starts bubbling.  
The heating must be stopped when the product starts changing from yellow to orange.
Quantitatively, about 5.4% of the initial material must be removed.
The final product is viscous, yellow, transparent, stable for months and no water soluble (Flasks can be cleaned by boiling diethylene glycol).

c) Product 477

Mix: 1 mole Terephthalic Acid (166 g)  
2 mole $\text{H}_3\text{PO}_4$ (85%)  (230 g)  
40 g epoxy (DOW: DEN-431®)
Mix and heat. Heat to about 80 oC and wait for bubbling. After high bubbling stop heating. The removed material is only about 1%. The product is yellow, turbid, not highly viscous and can separate in two phases after some time (1-3 days). However, it can be easily homogenized again by good mixing.

3) Foam-In-Place Procedure

In a small beaker (30 ml) mix:
  3.9 g solution VI  
  4.2 g solution XIII  
  2.7 g product 477  
  1.2 g Azodicarbonamide
Foam in HTS (Heat Transfer Salt) bath or in oven at T= 140 oC (takes about 2 min.). The product is a yellow foam (about 35-40 ml), nonflammable, flexible, stable for several days (at least 10). The foam doesn’t lose its properties when heated during two hours in basic media (NaOH, 20%), acid media ($\text{H}_3\text{PO}_4$, 85%) or water.
4) Similar Foams Systems: Other foams can be produced introducing the following changes:

a) Replace the Azodicarbonamide by CaCO₃. The obtained foam is white, nonflammable, good volume but lots less flexible than the described in part 3).

b) Reduce the solution XIII to 2.9 g, the Epoxy to 1 g, eliminate the Azodicarbonamide and use 0.8 g of Alumina Trihydrate (ATH). The product is white, strong, nonflammable and exhibits higher density than the case 3).

c) Reduce the solution XIII to 3.5 g, the epoxy to 0.9 g and include 0.4 g of ATH. The product is similar to the obtained in case 3) but has higher density.

d) Reduce the solution XIII to 2.9 g, increase the epoxy to 1.4 g, eliminate the Azodicarbonamide but include 0.6 g of Antimony Trioxide (Sb₂O₃). The foam is less flexible and has lower volume than the obtained in case 3).

C- Foam 547 C

1) Ingredients

a) Product 546
b) Product DP-1
c) Plasticizer
2) Foam Component Preparation

a) Product 546

1 mole CYMEL-301  (390 g)
3 mole Urea  (180 g)

Heat and mix strongly. Mix (at about 90 °C) for about 10-15 min. to get dissolution of the Urea. The final product is light yellow, highly viscous. When cooled down two phases can be formed. Top: liquid, yellow; bottom: yellow, solid (or semi-solid). Use even the top part or mix and heat to homogenize the product. Typically the material removed is 7.9 % of the original.

b) Product DP-1

Use: 2 mole H₃PO₄ (85%) (230 g)
1 mole Oxalic-2H₂O (126 g)

Heat and mix. At about 110-120 °C the material gets clear and bubbles. Allow it to bubble for about 2-4 min. Remove about 10-11% of the material (If too much material is removed the product can get a light pink color). When the material is cooled down it becomes a white solid (low melting point).

c) Plasticizer

Mix : 2 mole H₃PO₄ (85%) (230 g)
1 mole Oxalic-2H₂O  (126 g)
Heat and stir. At about 110-130 °C the material gets clear and bubbles. Let it bubble for some time. Remove about 30-31% of the initial mass. Cool down.

Then add 2 mole Ethylene Glycol (124.1 g) and heat to 120-140 °C. Let it bubble and remove about 54% of the mass of Ethylene Glycol added. Remove enough material to get a brown product (If the material remains yellow due to poor removal of water, etc. the results are not the expected).

3) Foam-In-Place Preparation

In a small beaker (100 ml) mix:

a) 9 g product 546
   3 g epoxy (DEN-431)
   0.3 g hydrazine

Stir and pre-heat this mixture to about 70 °C.

b) In another beaker mix:
   7 g product DP-1
   7 g plasticizer

Stir and pre-heat to about 70 °C.

Keep stirring the mixture a and pour on it the mixture b. Only about a half of the material b is required for instant foaming. However the quantity of the product b does not affect too much the properties of the foam.

The obtained foam is yellow (or yellow-green), flexible, nonflammable, the volume is about 70 ml. After some time (about 1 day) starts loosing its flexibility, and finally becomes rigid (but not brittle).
4) Similar Foam Systems

Several other foams can be produced by small changes in the formulation as follows:

a) The quantity of product b (mixture DP-1 and plasticizer) can be drastically changed without drastic changes in the foam. A small change (to 6 g DP-1 and 6 g plasticizer) doesn't make any difference because due to the fast cross-linking of the foam not all the product b can be poured into the mixture a. Quantities as 2.5/2.5, 5.0/5.0 and 7.5/7.5 g DP-1 /g plasticizer were used with similar results. However for the lowest values (2.5/2.5) the foam's density is drastically increased. For the highest values (7.5/7.5) the foam is sticky for some minutes (however, if it is put in the oven, in order to eliminate this inconvenient, it becomes rigid).

b) The product b can be replaced by the following mixture:

6 g DP-1
8 g of the product obtained when TMPO₄ (Trimethyl phosphate) and Ethylene Glycol are mixed and heated until removing about 6% of the total mass.

However in this case the foam exhibits higher density than in the case 3 and also gets rigid lots faster (less than 1 hour).

c) Foam can be also produced with the following formulations:

9 g product 546
2 g epoxy (DN-431)
Mix, preheat (to 70-80 °C) and add 8.3 g of DP-1. The product foams instantly, it is nonflammable, exhibits good volume but gets rigid in about 1 hour. Similar results are obtained if 1 g of epoxy is replaced by 1 g of the product prepared by mixing and heating 1 CYMEL/2 Bisphenol A until removing about 5.4% of the original mass. The epoxy can also be increased in the previous formulation but at about 4 g (rest of the components the same) the foam becomes flammable.

d) Many other foams have been prepared without using the plasticizer. In this case, the product is rigid when it is formed. Several formulations were tried including:

- Use DP-1.
- Use H₃PO₄ instead of DP-1.
- Use P₅O₅ instead of DP-1.
- Use a product prepared with 1 mole terephthalic acid and 2 mole H₃PO₄ (in different molar ratios), instead of DP-1.

e) Also some changes can be introduced to the original formulation by changing the Urea to TETA (triethylenetetraamine) or even reducing the Urea to 2 or 1½ moles. The disadvantages of these formulations compared with case 3 are even lower volume or lower stability.

D- Foam 375

1) Ingredients
a) DP-2
b) CYMEL-301
c) MEA

2) Foam Component Preparation

a) Product DP-2

Mix: 1 mole $\text{H}_3\text{PO}_4$ (85%) (115 g)
1 mole Oxalic acid-2$\text{H}_2\text{O}$ (126 g)

Stir and heat. At about 120 °C the material gets clear and bubbles. Allow it to bubble for 2-5 min. Remove between 5-10% of the initial mass. (If too much mass is removed the product can get a pink color). When the material is cooled down it becomes a white solid (low melting point).

3) Foam-in-place Procedure

In a small beaker (50 ml) put about 9 g of DP-2. Heat (to about 60-70 °C) and mix. In a 30 ml beaker mix 2.4 g MEA and 5.2 g of CYMEL-301. Heat to 60-70 °C. Pour the content of the second beaker to the first one. Instantly a foam is formed. It is orange, flexible, nonflammable, stable and exhibits good volume.

Note: This foam melts at about 200 °C

4) Similar Foam Systems

Several modifications can be introduced to the product 3 and still get a similar product, as follows:
a) React the product DP-2 with formic acid (1 mole of Formic by mole of H$_3$PO$_4$ used) and then react in the same way or even with plain CYMEL-301. The disadvantage is higher density than case 3.

b) React the product DP-2 first with Formic and then with ATH, (or even only with ATH). The disadvantage is higher density than case 3.

c) Mix and heat until bubbling:

4.6 g H$_3$PO$_4$
5.0 g Oxalic
1.2 g MEA

Then add 2.6 g CYMEL and 0.6 g Oxalic. Foam (in HTS bath, as described before). The obtained foam is orange, flexible, nonflammable, exhibits good volume but becomes brittle after a few days (typically 8-10).

**E- FOAM 549**

1) Ingredients

a) Plasticizer
b) DP-1.

2) Foam Component Preparation

a) Plasticizer
Mix:  2 mole H$_2$PO$_4$ (85%)  (230 g)  
1 mole Oxalic-2H$_2$O  (126 g)

Heat and stir. At about 110-130 °C the material gets clear and bubbles. Let it bubble for some time. Remove about 30-31% of the initial mass. Cool down the product.

Then add 2 mole of Ethylene glycol (124.1 g) and heat to 120-140 °C. Let it bubble until removing about 54% of the mass of ethylene glycol added. Remove enough material to get a brown product (if the material remains yellow due to poor removal of water, etc. the results are not the expected).

b) Product DP-1

Use:  2 mole H$_2$PO$_4$ (85%) (230 g)  
1 mole Oxalic-2H$_2$O (126 g)

Heat and mix. At about 110-120 °C the material gets clear and bubbles. Allow it to bubble for about 2-4 min. Remove about 10-11% of the material (If too much material is removed the product can get a light pink color). When the material is cooled down it becomes a white solid (low melting point).

3) Foam-In-Place Procedure

In a small beaker (100 ml) mix:

6 g CYMEL-301
1.6 g TETA (Triethylenetetraamine)
Add 16.8 g of plasticizer and finally
4.0 g DP-1 (this step is exothermic).
Mix and put about 10 g in a 30 ml beaker. Foam in HTS bath (about 150 °C) and then put it into the oven (110 - 120 °C). The product is flexible, stable, brown, has good volume and it's nonflammable.

Note: This foam melts at T< 200 °C.

4) Similar Foam Systems

Some changes can be introduced to the previous formulation, as follows:

a) Take 10 g of the formulation and add to it 1.5 g of CYMEL-301 and 0.6 g CaCO₃. Then foam as explained before. The foam is similar to the case 3, remains flexible for months but present some particles (CaCO₃ unreacted) as impurities.

b) The DP-1 can be eliminated, reducing the formulation to:

- 8.4 g plasticizer
- 0.8 g TETA
- 3.0 g CYMEL

The foam produced is similar to the case 3) but presents higher density.

F- Foam 513

1) Ingredients

a) Plasticizer
b) THEIC
c) CYMEL-301
2) Foam Component Preparation

a) Plasticizer

Mix:  2 mole H$_3$PO$_4$ (85%)  (230 g)
     1 mole Oxalic-2H$_2$O  (126 g)

Heat and stir. At about 110-130 °C the material gets clear and bubbles. Let it bubble for some time. Remove about 30-31% of the initial mass. Cool down the product.

Then add 2 mole of Ethylene glycol (124.1 g) and heat to 120-140 °C. Let it bubble until removing about 54% of the mass of ethylene glycol added. Remove enough material to get a brown product (if the material remains yellow due to poor removal of water, etc. the results are not the expected).

3) Foam-In-Place Procedure

In a small beaker (30 ml) mix:

6.1 g plasticizer
1.2 g THEIC (Trihydroxy ethyl isocyanurate)
2.9 g CYMEL-301

Foam in HTS (Heat Transfer Salt) bath at about 140 °C (takes about 2 minutes) and complete the curing (especially the top) in oven at 120-140 °C (can take until 10 minutes). The product is a brown foam, flexible, nonflammable, stable for many days (even months).

Note: This foam melts at T<200 °C
4) Similar Foam Systems

Some changes can be introduced to the previous formulation, producing similar results, as follows:

a) Include also Azodicarbonamide (0.1 g), CaCO₃ (0.2 g) or ATH (0.3 g), obtaining similar foams but some particles of these products remain (unreacted) in the foam.

b) Use 8 g of plasticizer: the product exhibits higher density than case 3).

c) Increase the CYMEL to 5.8 g: the foam also exhibits higher density than case 3).

d) Increase the plasticizer to 6.6 g and at the same time decrease the THEIC to 1.0 g and the CYMEL to 2.4 g: the product also presents higher density than case 3).

e) Use also Melamine (0.5 g) or Oxalic acid (0.5 g), increasing the CYMEL: the foam also exhibits higher density than case 3.

f) Replace THEIC by Melamine (formulation: 7.5 g plasticizer; 1.6 g CYMEL; 0.4 g Melamine or 7.0 g plasticizer; 1.6 g CYMEL; 0.8 g oxalic and 0.4 g Melamine). In these cases also the density is higher than the obtained in case 3).
G- FOAM P-100

1) Ingredients
   a) CYMEL-301\textsuperscript{R}
   b) Fomblin Z-Dol
   c) Diethyl oxalate (or dimethyl oxalate)

2) Foam Component Preparation
   a) Component A
   Place 7.8 g of CYMEL-301 and 2 g of Fomblin Z-Dol in a beaker or reaction flask: the two liquids are inmiscible. Heat with slowly stirring at 120 °C for 10-15 minutes: the substances undergo a transesterification reaction with evolution of (gaseous) methanol. The product is liquid, transparent, stable on storage (for months), and miscible with ingredient c), which serves as a blowing agent.

3) Foaming-In-Place procedure
   The foaming-in-place is effected by mixing the two components and heating for 1-2 minutes at 100-120 °C. Carbon dioxide and methanol, which are evolved in the reactions, act as the blowing agents. Alternatively a one-component system may be formed by mixing the two Components at ambient temperature. A single-phase system forms, which is stable upon storage and can be made to foam-in-place by heating at 100-120 °C for 1-2 minutes.
4) Similar Foam Systems

Other foams with similar characteristics were produced by replacing partially the Cymel by solution VI (2 mole CYMEL/1 mole Bisphenol A) or solution XIII (3 mole CYMEL/1 mole THEIC). However, these products do not exhibit better characteristics than the foam obtained in case 3).
PREPOLYMER FOR FOAM 547C: 1 MOLE CYMEL + 3 MOLE UREA
PREPOLYMER FOR FOAMS BL-1, and 510:

2 MOLE CYMEL + 1 MOLE BISPHENOL-A.
VII- DISCUSSION OF RESULTS

A- Evaluation of Foam Characteristics

Due to the tremendous quantity of different products (near 2,000) developed in this research, only qualitative analysis has been used to evaluate the characteristics of the foams and to select the most promising products. The basic evaluation of the main characteristics has been as follows:

1) Ease of foaming: this parameter was indirectly evaluated in terms of the time and temperature required for getting a crosslinked (or cured) foam. For the case of "instantly" foaming systems the time (generally a few seconds) was not measured. For the case of foams which require heating for some time for the appropriate curing, fixed temperatures was used in all the cases, as follows: about 140 °C for the HTS bath and about 120 °C for the oven. So, only the time (from a few seconds to several minutes) was required as parameter for the "foamability".

Only systems with foaming times lower than two minutes (under the above mentioned conditions) were considered as useful. This criteria forced us to reformulate, speed-up, or even eliminate many systems.

2) Foam density: the volumes of the different foams were easily compared because in almost all the formulations (excepting the instantly foaming systems) about 10 g of the pre-polymers and 30 ml beakers were used. So, simply checking the height reached by each system gave a good
measure for volume and specific gravity. More detailed evaluation of these parameters has also been executed for some cases but, considering that in many cases the foams didn't exhibit a good homogeneity, this basic test was considered as good enough.

3) Open vs. Closed-cell foams: There are two main classes of foams: open-cell and closed-cell foams. Open-cell foams correspond to the case in which the gas is in a continuous phase (115), meaning that the cells communicate. Closed cell foams correspond to the case in which the gas is discontinuous, forming discrete cells (115) in which the gas is perfectly encapsulated. The foaming process involves competition between the nucleation and growth of gas bubbles and the polymerization and/or crosslinking reactions. The reaction exotherm (or external heating of the system) encourages bubble growth, but the increasing viscosity of the gelling polymer restrains bubble growth (140). In terms of the foaming dynamics, a closed-cell foam is the case in which the bubble growth is slower than the viscosity increase so that the gas-filled cells remain separate. On the contrary, open-cell foam is the case in which the growing bubbles pierce the cell walls so that the open spaces become continuous.

For successful foam generation, a good balance has to be maintained between the polymerization and foam expansion reactions. If the polymer is not strong enough to contain the growing gas, bubbles boiling* and

* "Boiling" is said to occur in the foaming reaction when the rate of formation and/or release of the blowing agent (CO₂, etc.) is much greater than the polymerization rate. The result is a vigorous evolution of gas from the liquid froth that may end in foam collapse (140).
foam collapse can occur (140). On the other hand, if the crosslinking reaction is too fast, the cell walls will thicken and prevent the gas from expanding the foam to the proper density (140).

The degree of communication between the cells is responsible for a number of the characteristic properties of cellular plastics (115). Closed-cell foams exhibit low thermal conductivity and low water absorption, whereas open-cell foams have better acoustic insulation properties and cushioning characteristics.

In general, flexible foams tend to have open-cell structures while rigid foams tend to have closed-cell structures (115,140), but there are many exceptions to this rule. Figures VII-1 and VII-2 are low-magnification Scanning Electron Microscopy photographs of typical open-cell foams obtained in this research (Foam 547B).

Cell size and geometry are governed by the changing rheology of the wet foam and by the type of mixing, heating and/or entraining equipment that is used. In most commercial foam systems, specific surfactants are used to control cell morphology (8,115,140). These surfactants control the size of the foam cells by stabilizing the gas bubbles formed during nucleation or by reducing surface tension, improving nucleation and reducing cell size. Chemically these surfactants are organosiloxanes or silicone-based surfactants (8).

In this preliminary phase of our new foam synthesis project no surfactants have been used because the basic objective was to identify the most
FIGURE VII-1  Foam 547 C. S.E.M.  Magnification:35.

FIGURE VII-2  Foam 547 C. S.E.M.  Magnification:50.
promising chemical structures for nonflammable and thermally stable foams. Improvement of the physical properties of the resulting foams will be considered at the subsequent steps of the project. However, in some cases foams with small homogeneous cells, similar to commercial foams, were obtained.

4) Flexibility: the basic test used for this characteristic was also really simple, based on exerting pressure (with the finger) on the foam (no remotion of the beaker was required) and testing the displacement produced and the final effect. In some cases the foam was "destroyed" with this basic test and in such case it was classified as brittle and not considered for further tests.

Standardized tests for flexible foams such as ASTM D-3574-86: determination of compression set and determination of compression stress/strain characteristic and value are commercially used (8).

5) Nonflammability: a simple test, which we will call "The BIC Flammability Test", using a small quantity (typically 0.3-0.7 g) of the foam, and trying to burn it with a lighter has been used. With the results in this test the foams have been classified as nonflammable (166 products) and flammable (the rest).

Regarding LOI, as defined in ASTM D 2863-87* (72), no studies of this type were included (should be used in the next steps of this project)

* "Standard Method for Measuring the Minimum Oxygen Concentration to Support Candle-like Combustion of Plastics (Oxygen Index)"
because, considering the high quantity of samples involved the qualitative analysis for flammability mentioned before was considered more appropriate.

There are several other standardized small-scale tests and some large-scale tests (124,141) for flammability of plastics and cellular foams, such as:

- ASTM E-84, UL 723: known as the 25-foot tunnel test (124).
- ASTM D-2843: regarding smoke production (124).
- UL-94 flame test, NBS smoke density (142).

These tests were not used in this work for the same reasons discussed for the LOI test.

6) Thermal Stability: Another characteristic studied is the thermal stability, for which TGA was used (see results in Figures VII-3 to VII-17). TGA is a technique which measure the mass of the material (polymer) remaining when it is gradually heated to a given temperature, generating a curve of mass vs. temperature. TGA for polymers are normally made in air, nitrogen or oxygen. In this case both air and N₂ were used. However, this type of analysis was only executed to a few foams (considered the most representative) because this analysis is time consuming. The results showed that these polymers have excellent thermal stability (lots better than PUR
FIGURE VII-3  TGA FOR FOAM 510 IN AIR AND N₂
Sample: FOAM 547C AIR/N2
Size: 21.0306 mg
Method: CDA 200C-800C AT 5C/MIN
Comment: FLOW RATE 30 ML/MIN

TGA

File: FOAM547C.01
Operator: JDC
Run Date: 02/13/92 09:34

FIGURE VII-4 TGA FOR FOAM 547C IN AIR AND N₂
FIGURE VII-5  TGA FOR FOAM BL-1 IN AIR AND N$_2$
FIGURE VII-6  TGA FOR FOAM 510 COMPARED WITH PUR
FIGURE VII-7 TGA FOR FOAM 547C COMPARED WITH PUR
FIGURE VII-8 TGA FOR FOAM BL-1 COMPARED WITH PUR
FIGURE VII-9  TGA FOR FOAM 510 (AIR), INCLUDING FIRST DERIVATIVE
FIGURE VII-10 TGA FOR FOAM 510 (N₂), INCLUDING FIRST DERIVATIVE
FIGURE VII-11 TGA FOR FOAM 547C (AIR), INCLUDING FIRST DERIVATIVE
FIGURE VII.13  TGA FOR FOAM BL-1 (AIR), INCLUDING FIRST DERIVATIVE

Sample:  FOAM BL-1
Size:  24.5492 mg
Method:  CO2, 2000-600°C AT 50°C/MIN
Comment:  AIR FLOW RATE 30 ML/MIN

TGA V2.08 DuPont 9900

DERIVATIVE

Temperature (°C)

Weight (g)

Days
FIGURE VII-14 TGA FOR FOAM BL-1 (N₂), INCLUDING FIRST DERIVATIVE
FIGURE VII-16 TGA FOR PUR(AIR), INCLUDING FIRST DERIVATIVE
FIGURE VII-17  TGA FOR SOLIMIDER^R (AIR), INCLUDING FIRST DERIVATIVE
foams, as showed in Figures VII-6 to VII-8), with losses between 0 and 5% at 200 °C and remaining material between 40 and 47% at 800 °C (with nitrogen flow).

The TGA for Solimide is also included (Figure VII-17). This foam, corresponding to a commercial post-cured material, exhibits excellent thermal stability at temperatures below 500 °C. However, at about 570 °C the decomposition is evident, being the foams produced in this work (only post-cured at temperatures below 200 °C) lots better than the Solimide foam for temperatures above 600 °C.

B- Effect of Elemental Components on Flammability and other Characteristics

1) Flammability
In this section are going to be covered some general aspects regarding the formulations used for getting the nonflammable foams with the other required characteristics (see INTRODUCTION).

Only the nonflammable polymers (a total of 166) are going to be considered. Besides that, the formulations including fluorine compounds (even in small quantities) won't be considered in this review due to the very high cost of these compounds (commercially FOMBLIN® Z-DOL from Montefluos and KRYTOX® from DUPONT).
The elements considered as nonflammable in this review are: P, N (especially high quality), Al, Ca, Sb, Mg, and B. Two general cases are considered:
Formulations containing only P and N as nonflammable elements, and
Formulations including nonflammable elements different from P and N.

a) For the first case, formulations including only P and N as nonflammable elements, a total of 113 formulations were considered. The contents of P and N are mapped with "+" in the figure VII-18. For this case, the average content of P is 9.1%*, and the average content of N is 11.6%; the rest (79.3%) corresponds to C, O, and some H. So, relatively low contents of P+N (typically 15-25% as showed in figures VII-18 and VII-19) are required for achieving nonflammability.

The following "rule-of-thumb" can be formulated with these data:
A nonflammable material (with only P and N as nonflammable elements) requires about 20% of combined P and N in its molecule, being the content of P of about 9%. This "rule-of-thumb" has been successfully applied in this set of experiments to predict the behavior (flammability or nonflammability) of complex formulations.

b) For the case of compounds involving other nonflammable elements (typically Al, Ca but also Mg, Sb, and B), a total of 53 nonflammable formulations have been obtained. The contents of P and N are mapped with "*" in the figure VII-18. The average content of P and N is lower.

* These contents correspond to the non-cured material. For approximate composition of the cured foams they should be multiplied by 1.13.
FIGURE VII-18 PHOSPHORUS AND NITROGEN CONTENTS IN NONFLAMMABLE FOAMS.
FIGURE VII-20  NONFLAMMABLE FOAMS: CONTENT OF P + N + OTHER NONFLAMMABLE ELEMENTS.
(8% and 11.2%, respectively) than in the previous case. However, the total content of nonflammable elements is higher (23.7% vs. 20.7% for the previous case). In other words, considering the low (0.4%) decrease of N, a relatively low average reduction in the P content (1.1%) forces to introduce a relatively high percentage (average: 4.5%) of other nonflammable elements (Al, Ca, Sb, Mg,...). This confirms the "feeling", result of many experiments, that in this type of formulations the P is the best element for achieving nonflammability.

Other obvious classifications for these nonflammable products could be based on the type of P or N molecules involved. In this review the products are classified only based on the kind of P compound, and not based on the kind of N compound, due to two main reasons:

a) Almost all the products considered involved CYMEL-301 (a high quality nitrogen-containing compound described in Chapter V), so there wouldn't be possible classification.

b) There is no evidence in these results of differences in nonflammability when pure "high" quality N-containing compounds (from CYMEL-301, THEIC, ...) are used, compared with products containing "lower" quality nitrogen or both "high quality" and "lower" quality(from hydrazine, urea, melamine, caprolactam, ethyleneurea, MEA, DEA, TETA, ...).

Regarding the classification based on P, in the table VII-1 are summarized the main results. Five families of P compounds have been defined, according to the type of P-containing molecule involved. These families
TABLE VII-1  Characteristics of Foams According to their "Phosphorus-Containing Ingredient".

<table>
<thead>
<tr>
<th>TYPE</th>
<th>FLEXIBLE</th>
<th>RIGID</th>
<th>BRITTLE</th>
<th>HIGH DENSITY</th>
<th>LOW DENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMPO₄</td>
<td>36</td>
<td>4</td>
<td>8</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>(50)*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>18</td>
<td>4</td>
<td>10</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>(28)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP-1**</td>
<td>26</td>
<td>14</td>
<td>10</td>
<td>15</td>
<td>24</td>
</tr>
<tr>
<td>(56)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plastic.***</td>
<td>15</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>(17)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP-2****</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The numbers in parenthesis indicate the number of samples considered.
** DP-1: See Chapter VI, Section C.
*** Plasticizer: See Chapter VI, Section C.
**** DP-2: See Chapter VI, Section D.
are: $\text{H}_3\text{PO}_4$, $\text{TMPO}_4$, (trimethyl-phosphate), DP-1 (See Chapter VI), DP-2 (See Chapter VI), and plasticizer (see Chapter VI). The distribution by families of all the nonflammable foams is as follows:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{PO}_4$</td>
<td>16.9%</td>
</tr>
<tr>
<td>$\text{TMPO}_4$</td>
<td>30.1%</td>
</tr>
<tr>
<td>DP-1</td>
<td>33.7%</td>
</tr>
<tr>
<td>DP-2</td>
<td>1.8%</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>10.2%</td>
</tr>
<tr>
<td>Combinations, etc</td>
<td>Rest</td>
</tr>
</tbody>
</table>

2) Other characteristics
Statistically some conclusions can be made, based on the table VII-1, for other important characteristics of the foams, as follows:

a) Flexibility: Considering that 15 out of 17 (88%) of the foams prepared using the plasticizer were reported as flexible (at least a few minutes after their preparation), being this the highest percentage for all the families considered, it can be said that the plasticizer tends to produce flexible materials (foams). Similarly, 72% (36 out of 50) foams including $\text{TMPO}_4$ are flexible, so it can be also said that the $\text{TMPO}_4$ tends to produce flexible foams (relatively speaking).

On the contrary, DP-1 tends to produce rigid materials (14 out of 56, corresponding to 25% which is the highest percentage of all the considered families). Of course, many foams were classified neither as flexible nor as rigid because they were brittle, or they have parts flexible and parts rigid, etc.
b) Foam density: Regarding the foam volumes obtained with a given quantity of reagents it can be said that, again relatively speaking, the plasticizer (11 out of 17 products, corresponding to 64.7%) and the DP-1 (24 out of 56, corresponding to 42.8%) tend to generate foams with good volume (low density). On the contrary, the H₃PO₄ tends to produce low volumes (9 out of 28, corresponding to 32.1% of these foams exhibit this characteristic).

c) Strength: The H₃PO₄ shows a tendency to produce brittle materials (10 out of 28, equivalent to 35.7%).

d) Stability: Regarding this characteristic, it is important to mention that only a few flexible products have been stable for more than 10 days (an arbitrary limit); so, no conclusions can be made about the influence of the P type on this characteristic. The nature of this behavior (loss of flexibility) has not been completely determined.

Hydrolysis, a common phenomenon in the P containing compounds (101,102,143,144,145,146) which has drastically reduced the applicability of the P-containing polymers seems not to be the cause for the loss of flexibility (and even the transformation into brittle products). Before giving the reason for these conclusions it's necessary to consider carefully the hydrolysis phenomena. The literature is rich in references about hydrolysis of P compounds (101,102,143,144,145,146). Some P compounds, such as inorganic rubber ((Cl₂PN)₃₋₇) (101,143), polyhalophosphazenes (101), phosphorus oxynitride (143), oxyhalides (POX₃) (144,146), phosphorus trihalides (146), and phosphonitrilic
chlorides (146), hydrolize even with the air moisture. Other compounds, like phosphorus sesquisulfide (146) require higher temperatures (boiling water). Some others, such as linear polyphosphates (145), monoesters of orthophosphoric acid (146), and pyrophosphate ester (146) hydrolize fast in acid media (low pH). There are also some compounds, such as tripolyphosphates (146), which hydrolize faster at high pH (basic media). Some other compounds, like esters of phosphonic acids (145), pyrophosphite (146), and Graham's salt (146) which hydrolize easily even in acid or basic media but not at neutral pH. There are also some P compounds, like phosphate triesters (145), which hydrolize easily in any kind of media (acid, basic, neutral). Other P compounds which have been reported as hydrolytically unstable are: poly(diphenoxyphosphazene) (147), $P_4O_{10}$ (145), phosphite triesters (145), hypophosphoric acid (146), and pyro- and tripolyphosphates (146).

Two main conclusions can be obtained from this relatively long list:
i) It's clear that hydrolysis is common in P compounds.

ii) Hydrolysis increases with temperature and normally increases at low or high pH, depending on the compound.

Of course, with this wide variety of P compounds there are many different hydrolysis products. However, some of them characterize the hydrolysis phenomena because of the formation of drops or salts in the surface of the hydrolyzed compounds. This kind of characteristic products are:
i) $H_3PO_4$: produced in the hydrolysis of inorganic rubber (101,143), phosphorus oxynitride (143), $P_4O_{10}$ (145), phosphonitrilic chloride (146), hypophosphoric acid (146), and polyhophosphazenes (101).
ii) HCl, HBr, HF: produced by hydrolysis of oxyhalides (POX₃) (145,146), inorganic rubber (101,143), polyhalophosphazenes (101), and phosphorus trihalides (146).

iii) Salts like NH₄Cl: produced by hydrolysis of phosphonitrilic chlorides (146) and inorganic rubber (143).

As mentioned before, the loss of flexibility and even the transformation into brittle products which occurs in the polymeric foams discussed in this chapter seem not to be due to hydrolysis. The main reasons for these conclusions are:

i) As showed before, the hydrolysis of P compounds is drastically accelerated by high temperature, humidity and basic or acid media. However, some of the foams (especificly Foam 510) which exhibit the loss of flexibility don't show any change when heated to 100 ºC during two hours in: acid media (H₃PO₄, 85%), basic media (NaOH, 20%) or water. So, these foams seem to be hydrolytically stable.

Besides that, the behavior of most of the foams was similar, no matter if they were kept in vacuum, laboratory conditions or atmospheric conditions (normally higher humidities and higher temperatures). So, the content of moisture in the ambient and the temperature do not produce big changes in the behavior of the foams, which again lets us suppose that it is not hydrolysis which changes the characteristics of these foams.
ii) The typical hydrolysis products mentioned before (drops of $H_3PO_4$, HCl, etc. or salts as NH$_4$Cl) are not observed during the lost of flexibility or the transformation into brittle products.

Finally, it's important to mention that several nonflammable rigid foams have remained stable (it means, they have not become brittle) for long times (several months), which would make them useful for insulation applications.

C- Structure-Property Relations (Flexibility vs. Nonflammability and Thermal Stability)

One of the greatest difficulties found in this research has been to deal with two characteristics which in general terms are contradictory: flexibility and thermal stability.

In fact, at least for organic polymers stability and thermal stability are characteristics of polymers with:

- Aromatic rings
- Aromatic rings with functional groups
- Heterocyclic rings
- Ladder structures
In general the biggest disadvantage of these polymers is that they are difficult to process, so normally some flexibilizing units (such as ether, sulfone or alkylene groups), which can decrease dramatically the thermal stability (and consequently the nonflammability), have to be introduced in the polymer backbone. In other words, there is a compromise between processability and thermal stability/nonflammability. For this reason, although relatively many different polymers have been reported as thermally stable and/or nonflammable (see table II-2), only a really few ones can be converted into flexible foams.

Similarly, in this work many stable nonflammable and thermally stable rigid foams have been produced and only a few flexible nonflammable and thermally stable foams (some of them with stability problems) have been obtained. This is explained by the contradictory requirements between thermal stability (and nonflammability) and flexibility. Some very stable, low cost, rigid, nonflammable foams developed during this work can have applications in thermal insulation.
VIII- A CLOSER LOOK INTO PHOSPHORUS CHEMISTRY

Considering that in this research phosphorus was the most effective non-flammable element, a brief review of its chemistry is in order. This may help us to understand the structure of some of our foam system components, their subsequent transformation into the polymer networks that constitute the foam systems, and partially the foam characteristics.

A- Background

In the last three decades the knowledge of phosphorus compounds has expanded so rapidly that it now constitutes a major branch of chemistry (145). During these years there has been a great increase in the volume and diversity of the commercial applications of P compounds (145). These applications are in the following fields (145): animal foodstuffs, dental materials, detergents (synthetic detergents), electrical materials, fertilizers (being the largest single application), flame retardants, food additives, glass, luminescent phosphorus, matches, medicines, metal treatment, nerve gases, oil additives, pesticides, pigments, plastics, refractories, surfaceness, water treatment.

The leading industrial chemical is phosphoric acid and the inorganic compounds remain the most important (145).

Phosphorus is not found free in nature and almost always occurs in the fully oxidized state (+5) as phosphate. It is widely distributed in this form in soils, rocks, oceans, all living cells, etc. (145).
More than 200 different phosphate minerals are known but only those in the apatite group (fluorapatite, chlorapatite, hydroxyapatite) occur in sufficient abundance and concentration to be useful as commercial sources of P (145). Although P exists in nature almost exclusively in the +5 oxidation state, as showed in table VIII-1 (145) several other oxidation states are possible.

![Chemical structures and oxidation states](image)

**TABLE VIII-1** Oxidation States of Phosphorus Compounds.

For this research, compounds with the highest (+5) oxidation state were selected (orthophosphoric acid, phosphates, etc) because pentavalent P cannot be further oxidized by combustion, so it confers the nonflammability to its compounds.
In general, P compounds tend to react by electron-pair mechanism, utilizing the nucleophilic reactivity of the lone-pair electrons in the case of trivalent compounds, and the electrophilicity of the phosphorus atom in pentavalent derivatives (145). Besides that, some P reactions proceed by a free radical mechanism (145).

Bonds of P with many other elements have been reported. Table VIII-2 (145) shows some representative bond lengths for P compounds.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length</th>
<th>Compound</th>
<th>Bond</th>
<th>Length</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>P–H</td>
<td>1.44</td>
<td>PH₃</td>
<td>P–O</td>
<td>1.64</td>
<td>P₄O₆</td>
</tr>
<tr>
<td>P–F</td>
<td>1.57</td>
<td>PF₃</td>
<td>P–O⁻</td>
<td>1.54</td>
<td>LiH₂PO₄</td>
</tr>
<tr>
<td>P–Cl</td>
<td>2.04</td>
<td>PCl₃</td>
<td>P==O</td>
<td>1.45</td>
<td>POCl₃</td>
</tr>
<tr>
<td>P–Br</td>
<td>2.22</td>
<td>PBr₃</td>
<td>P–P</td>
<td>2.22</td>
<td>P₂H₄</td>
</tr>
<tr>
<td>P–I</td>
<td>2.52</td>
<td>PI₃</td>
<td>P≡P</td>
<td>2.03</td>
<td>(C₁₈H₂₉)P³⁻</td>
</tr>
<tr>
<td>P≡B</td>
<td>1.96</td>
<td>PB</td>
<td>P≡P</td>
<td>1.87</td>
<td>P₂</td>
</tr>
<tr>
<td>P≡B</td>
<td>1.83</td>
<td>(Mes)₂B=PMes</td>
<td>P–Si</td>
<td>2.27</td>
<td>SiP</td>
</tr>
<tr>
<td>P≡C</td>
<td>1.85</td>
<td>PMe₃</td>
<td>P–Ge</td>
<td>2.31</td>
<td>P(GeH₃)₃</td>
</tr>
<tr>
<td>P≡C</td>
<td>1.66</td>
<td>Ph₃P=CH₂</td>
<td>P–Sn</td>
<td>2.53</td>
<td>P₂(SnPh₃)</td>
</tr>
<tr>
<td>P≡P</td>
<td>1.54</td>
<td>HCP</td>
<td>P–S</td>
<td>2.09</td>
<td>P₄S₃</td>
</tr>
<tr>
<td>P=N</td>
<td>1.77</td>
<td>Na₅P₂O₆NH₂</td>
<td>P≡Se</td>
<td>2.24</td>
<td>P₄Se₃</td>
</tr>
<tr>
<td>P≡N</td>
<td>1.57</td>
<td>Ph₃P≡C₆H₄Br</td>
<td>P≡Se</td>
<td>2.24</td>
<td>P₄Se₃</td>
</tr>
<tr>
<td>P≡N</td>
<td>1.49</td>
<td>PN</td>
<td>P≡Se</td>
<td>1.96</td>
<td>Et₃PSe</td>
</tr>
</tbody>
</table>

TABLE VIII-2 TYPICAL BOND LENGTHS FOR PHOSPHORUS COMPOUNDS.

B- Phosphoric Acid and Phosphates

Phosphates are compounds which contain P-O linkages. Such compounds may have three, four, five or six oxygen atoms linked to a central P atom (see fig. VIII-1) (145).

FIGURE VIII-1 Types of Phosphates.
However, the most common phosphates are those in which the P atoms are surrounded tetrahedrally (or at least approximately so) by four oxygen atoms (145,146). The phosphates can be called normal if only P-O linkages oxygens are replaced by other atoms or groups (145).

The most used P chemical is phosphoric acid (H₃PO₄), also called monophosphoric acid or orthophosphoric acid. It is commercially produced by reaction of apatites with sulfuric rock. Other phosphoric acids are (145):

![Orthophosphoric acid](image)

![Pyrophosphoric acid](image)

![Tripolyphosphoric acid](image)

![Polyphosphoric acid](image)
Orthophosphoric acid has only one strongly ionizing hydrogen atom. The dissociation scheme can be represented as (145):

\[
\begin{align*}
\text{HOPO}_3^+ + \text{H}_2\text{O} & \rightleftharpoons \text{HOPO}_3^- + \text{H}_3\text{O}^+ & K_1 = 7.52 \times 10^{-3} \\
\text{HOPO}_3^- + \text{H}_2\text{O} & \rightleftharpoons \text{HOPO}_3^- + \text{H}_3\text{O}^+ & K_2 = 6.23 \times 10^{-8} \\
\text{HOPO}_3^- + \text{H}_2\text{O} & \rightleftharpoons \text{HOPO}_3^- + \text{H}_3\text{O}^+ & K_3 = 2.2 \times 10^{-13}
\end{align*}
\]

Since the first dissociation constant \((K_1)\) is much larger than the others, very little of the material dissociates as showed in the second and third reactions.

Polyphosphoric acid can be derived, from ordinary orthophosphoric acid, by abstraction of water as follows (145):

\[
\begin{align*}
\text{HOPO}_3^- + \text{HOPO}_3^- & \rightarrow \text{HOPO}_3^-\text{HOPO}_3^- + \text{H}_2\text{O} \\
\text{HOPO}_3^- + \text{HOPO}_3^- & \rightarrow \text{HOPO}_3^{-}\text{HOPO}_3^- + \text{H}_2\text{O} \\
\text{(n-1)POCl}_3 + (2n+1)\text{H}_3\text{PO}_4 & \rightarrow 3\text{H}_{n+2}\text{P}_{n+1}^\text{O}_{3n+1} + 3(n-1)\text{HCl}
\end{align*}
\]

The general formula for polyphosphoric acid is \(H_{n+2}P_nO_{3n+1}\) (108), being the more known the diphosphoric (or pyrophosphoric acid), \(H_4P_2O_7\), and the triphosphoric acid, \(H_5P_3O_{10}\).
Also many polyphosphates have been reported, which can be classified as diphosphates \((n=2)\), triphosphates \((n=3)\), tetraphosphates \((n=4)\), oligophosphates \((4<n<50)\) and long chain phosphates \((n>50)\) (145). Also some rings have been reported (145).

C- Polyphosphazenes

The most studied P-containing polymers (excepting the case in which P compounds act only as flame retardant) are the polyphosphazenes.

Polyphosphazenes are compounds with the group \(\text{P}=\text{N}-\), they can be linear or cyclic and can have pendant groups such as halogen elements or organic groups (145).

Polyphosphazenes are materials with excellent flame-retardancy due to its high contents of P and N (148). So, in general terms these compounds have similarities with the polymers obtained in this work. In fact, poly(arylophosphazenes) with LOI as high as 65 have been reported (101).

Three types of polymers based on phosphazene structures have been developed, as follows (148): 1) linear-type polymers, 2) cyclolinear polymers, and 3) cross linked cyclomatrix polymers (148).

1) Linear polyphosphazenes
These polymers have the following general structure (148):
in which R is normally H, an halogen element or an organic group.

Two evident modification of the linear structures are branch formation and crosslinking.

The most important linear polyphosphazenes are: a) linear poly(dihalophosphazenes) (case in which R is an halogen element), and b) linear organophosphazene polymers (case in which R is an organic group).

a) Poly(dihalophosphazenes)
The linear poly(dihalo)phosphazenes are:

i) poly(difluoro-phosphazene), (NPF₂)_n, which is prepared by thermal polymerization of the trimer or tetramer, (NPF₂)₃ or ₄, in a high pressure system at 350 °C for 15 hours or longer (148). It is a colorless, or pale amber elastomer. One of the unusual properties of (PNF₂)ₙ is its low temperature elasticity (from about -70 °C to 350 °C). (148). However the polymer is not useful due to its high sensitivity to hydrolysis (decomposition is evident after a few minutes exposure to a moist atmosphere) (148).

ii) Poly(dichlorophosphazenes): they can be prepared by reacting PCl₅ with NH₄Cl (145) or by thermal polymerization of cyclic chlorophosphazenes (148). The product is a soft, colorless transparent,
soluble elastomer, which can be crosslinked by prolonged polymerization (148). This product has been known as "inorganic rubber" (101,143) or "phosphonitrilic rubber" but due to its degradation in contact with water or atmospheric moisture has not had practical applications (101). The degradation starts with the hardening of the elastomer (due to crystallization and crosslinking) and conversion to inorganic products such as HCl, NH₄Cl, ammonium phosphate or phosphoric acid (148).

iii) Poly(dibromophosphazene): this polymer, with formula (NPBr₂)ₙ, is an amber-colored rubbery, tough, material which is prepared by thermal polymerization of the cyclic trimer or tetramer (148). It exhibits rubber elasticity between -15 and 270 °C. This polymer is also hydrolytically instable.

iv) Poly[bis(isothiocyanophosphazene]: this polymer is classified in this group due to its similar properties compared with the poly(dihalophosphazenes). Its formula is [NP(NCS)₂]ₙ and is synthesized by polymerization of the cyclic trimer or tetramer, [NP(NCS)₂]₃ or ₄. The contact with moisture results in decomposition and crosslinking of the polymer.

b) Linear organophosphazene polymers

Different linear poly(organophosphazenes) have been prepared. These include poly(alkoxy- and aryloxyphosphazenes), poly(alkyl- and arylphosphazenes) and poly(aminophosphazenes)(148). Commonly these polymers are synthesized by replacement of halogen atoms in
poly(dichlorophosphazenes) by organic groups (148) which make them more useful due to improved hydrolytic stability (145). However, its flame retardance can be decreased because these organic pendant groups are flammable. But, on the other hand, the residual P-halogen groups would be easier to hydrolyze (144).

The following is a list of some of the poly(alkoxyphosphazenes) and poly(aryloxyphosphazenes) which have been synthesized (148):

\[ [\text{NP(OMe)}_2]_n, \ [\text{NP(OE}t)_2]_n, \ [\text{NP(OCH}_2\text{CF}_2\text{CF}_2\text{H})_2]_n, \ [\text{NP(OCH}_2\text{C}_2\text{F}_3]_n, \ [\text{NP(OCH}_2\text{-CF}_3]_n, \text{ and [NP-(OPh)]}_n. \]

Some of these polymers exhibit excellent properties, so they are considered high performance polymers (149). Some of these materials and their properties are:

i) Poly[bis(methoxy)phosphazene]: its formula is \([\text{NP(OMe)}_2]_n\) and it is a colorless, rubbery material, stable to water but soluble in some organic solvents (methanol, chloroform, dioxane, etc.). Besides that its thermal stability is low (148).

ii) Poly[bis(ethoxy)phosphazene]: its formula is \([\text{NP(OE}t)_2]_n\), it is a colorless elastomer, with low thermal stability but it is hydrolytically stable.

iii) Poly[bis(phenoxy)phosphazene]: This is a polymer with formula \([-\text{NP(OPh)}_2\_]_n\), prepared by the interaction of poly(dichlorophosphazene) with sodium phenoxide (148). It's hydrolytically stable, resists acid and
basis attack, it is nonflammable but degrades at high temperature (148), showing a weight loss at temperatures above 300 °F (147).

iv) Poly[bis(trifluoroethoxy)phosphazene]: its formula is [-NP(OCH$_2$CF$_3$)$_2$-]$_n$, is one of the polyphosphazenes with best characteristics. Fibers and films with excellent tensile strength can be prepared with this material. The solid polymer is unaffected by water, glacial acetic acid, concentrated sodium hydroxide solutions, alcohols, and pyridine but it is soluble in some organic solvents such as acetone, ethylene glycol, ethyl acetate, methyl ethyl ketone, etc. (148). The thermal stability of this polymer is relatively good.

v) Poly[bis(pentafluoropropoxy)phosphazene], [-NP(OCH$_2$C$_2$F$_5$)$_2$-]$_n$, is prepared by reaction of poly(dichlorophosphazene) with sodium 2,2,3,3-pentafluoropropoxide. It exhibits good resistance to hydrolysis and thermal resistance, and it is insoluble in most organic solvents. (148).

vi) Poly[bis(2,2,3,3-tetrafluoropropoxy)phosphazene]: this polymer has formula [-NP(OCH$_2$CF$_2$C$_2$F$_2$H)-]$_n$, is a soft, transparent, film forming material. It's stable to water and aqueous media (148).

vii) Poly(trifluoroethoxy-heptafluorobutoxyphosphazene) copolymer: [-NP(OCH$_2$-CF$_3$)(OCH$_2$C$_3$F$_7$)-]$_n$. This is a white rubbery elastomer, resistant to boiling water, common organic solvents, concentrated sulfuric acid or concentrated potassium hydroxide solutions. When held in flame
the polymer softens but it does not burn. Softening of the material occurs near 175 °C (148).

Poly(diaminophosphazenes)

There are three principal classes of poly(diaminophosphazenes) (148), as follows:
Bis(primary amino) derivatives (I), bis(secondary amino) derivatives (II), and mixed primary-secondary amino polymers (III).

\[
\begin{align*}
\text{I} & : \begin{array}{c}
\text{NHR} \\
\text{NHR}
\end{array} \\
\text{II} & : \begin{array}{c}
\text{NR}_2 \\
\text{NR}_2
\end{array} \\
\text{III} & : \begin{array}{c}
\text{NR}_2 \\
\text{NHR}
\end{array}
\end{align*}
\]

All of these polymers are synthesized by the interaction of poly(dichlorophosphazene) with a primary or secondary amine.
i) Primary amino derivatives: Several primary amino-substituted polymers with general structure \([\text{NP(NHR)}_2]_n\) have been prepared in which NHR is NHMe, NHet, NHPr, NHBu, and NHPH (148). These primary amines can act as cross-linking agents.
In general the primary aminophosphazenes are less flexible materials than the poly(alkoxyphosphazenes) discussed earlier. No evidence for hydrolytic instability has been observed with these polymers (148).
ii) Secondary amino derivatives: secondary amino polymers such as [NP(NMe₂)₂]ₙ, [NP(NC₅H₁₀)₂]ₙ, and [NP(NC₄H₈)₂]ₙ, have been prepared (148); these materials are stable to hydrolysis.

iii) Mixed Diethylamino-aminophosphazene polymers: these polymers can be prepared by replacing approximately one-half of the available chlorine atoms of poly(dichlorophosphazene) with diethylamine, and then substitute the remaining halogen atoms by a different amine, to yield copolymers. Examples of these polymers are: [NP(NEt₂)(NHEt)]ₙ, and [NP(NEt₂)(NHPr)]ₙ; however, these polymers hydrolyze slowly, with liberation of ammonia.

2) Cyclolinear polyphosphazenes

The development of this field has resulted from the attempts to use the high thermal stability of cyclotri- or cyclotetra-phosphazene rings but, at the same time, introduce some flexible units in the polymer. The lower cyclophosphazenes are rigid so they must be linked by flexible units to avoid the formation of rigid, insoluble materials.

Several types of reactions have been used to achieve this, as follows: condensation-type reactions, dehydrochlorinations, denitrogenation of azides, transesterifications, and radiation-induced reactions (148). Examples of these products are (148):
**FIGURE VIII-2 Examples of Reactions of Cyclolinear Phosphazenes:** a) Condensation, b) Transesterification.

3) **Cyclomatrix polymers**

Phosphazene cyclomatrix polymers are prepared by the cross-linking of cyclic trimeric or tetrmeric rings to yield rigid, insoluble, high melting resins (148). Their applications include surface coatings, wire enamels, textile treatment agents, and structural polymers.

**D- The P-P bond**

1) **History**
Considering that elemental phosphorus contains P-P bonds, the history of this topic might be said to date back to the twelfth century when an Arabian alchemist probably discovered white phosphorus. However, most authorities in this topic agree that elemental P was first described by the seventeenth-century alchemist Henning Brand (150). With modern
structural techniques it has been possible to discover that white phosphorus consists of discrete regular tetrahedra of P atoms (150).

The relatively tardy development of the chemistry of the P-P bond (compared with other elements in the same group) is partially due to the instability (and intractability) of many polyphosphorus species. The instability does not derive from thermodynamic factors (150) because the P-P (51.3 Kcal/mole) and S-S (50.9 Kcal/mole) single bond energies are similar. The problem of instability has its origins in the higher probability of nucleophilic and electrophilic attack compared with the S-S and As-As bonds.

2) Structures
Many different P-P containing compounds have been prepared. A descriptive list (neither exhaustive, nor comprehensive) is showed in table VIII-3 (150). For our case, especial importance is given to the oxyacids. The characteristic P-P bond lengths for different compounds are showed in table VIII-4 (150).

3) Synthetic routes to the P-P bonds
In 1877 Kohler and Michaelis treated polyphosphine with phenyldichlorophosphine, producing the P-P bond. This reaction pioneered the synthetic route to this type of compounds, and it is still used with a small change consisting on the addition of a tertiary amine which serves as a hydrogen halide acceptor (150). Another important synthetic method is based on the reaction of phosphorus halides with active metals (150). Even a tertiary phosphine can replace the active metal by serving as halogen acceptor.
TABLE VIII-3 COMPOUNDS CONTAINING P-P BONDS.

Elemental Phosphorus

\[
\begin{align*}
\text{white} \\
(\text{tetraphosphorus})
\end{align*}
\]

Phosphorus Sulfides

\[
\begin{align*}
P_4S_3 & \quad & P_4S_5 & \quad & P_4S_7
\end{align*}
\]

Acyclic Polyphosphines, \( P_4R_{P+1} \)

\[
\begin{align*}
\text{diphosphone} & \quad & \text{triphosphone} & \quad & \text{diphosphone disulfide}
\end{align*}
\]

Compounds with Donor–Acceptor Bonds

\[
\begin{align*}
\text{phosphine–phosphorane} & \quad & \text{phosphine–phosphinidine}
\end{align*}
\]

Oxy and Thio Acids and their Esters

\[
\begin{align*}
\text{diphosphorous acid} & \quad & \text{hypophosphoric acid} & \quad & \text{hexathiohypophosphoric acid}
\end{align*}
\]

Cyclopolyphosphines, \( P_4R_n \)

\[
\begin{align*}
\text{cyclotriposphine} & \quad & \text{cycлотetraphosphine}
\end{align*}
\]
### Table VIII-4  P-P Bond Lengths

<table>
<thead>
<tr>
<th>Molecule or Ion</th>
<th>Bond length, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{P}_2\text{I}_4$</td>
<td>2.21 ± 0.06</td>
</tr>
<tr>
<td>$(\text{C}_2\text{H}_5)_2\text{P}(\text{S})\text{P}(\text{S})(\text{C}_2\text{H}_5)_2$</td>
<td>2.22 ± 0.01</td>
</tr>
<tr>
<td>$(\text{CH}_3)(\text{C}_6\text{H}_5)\text{P}(\text{S})\text{P}(\text{S})(\text{C}_6\text{H}_5)(\text{CH}_3)$</td>
<td>2.21</td>
</tr>
<tr>
<td>$(\text{CF}_3\text{P})_4$</td>
<td>2.213 ± 0.005</td>
</tr>
<tr>
<td>$(\text{CF}_3\text{P})_5$</td>
<td>2.223</td>
</tr>
<tr>
<td>$(\text{PO}_2)_6^{6-}$</td>
<td>2.20 (avg.)</td>
</tr>
<tr>
<td>$\text{P}_4\text{S}_3$</td>
<td>2.235 ± 0.005</td>
</tr>
<tr>
<td>$\text{P}_4\text{Se}_3$</td>
<td>2.25</td>
</tr>
<tr>
<td>$\text{P}_4\text{S}_5$</td>
<td>2.21 ± 0.025</td>
</tr>
<tr>
<td>$\text{P}_4\text{S}_7$</td>
<td>2.35 ± 0.01</td>
</tr>
<tr>
<td>$\text{P}_4\text{S}_3\text{I}_2$</td>
<td>2.21 ± 0.04</td>
</tr>
<tr>
<td>$\text{P}_4$</td>
<td>2.21 ± 0.02</td>
</tr>
<tr>
<td>Black phosphorus</td>
<td>2.18</td>
</tr>
<tr>
<td>$\text{P}_2(\text{CH}_3)_4 \cdot 2\text{BH}_3$</td>
<td>2.205 ± 0.004</td>
</tr>
</tbody>
</table>
There are several other reactions, some of them using red or white phosphorus, Grignarg reagents, etc., useful for producing P-P bond-containing compounds.

For the case of P-P acids and their salts, also some synthetic routes have been reported. Hypophosphoric acid (H₄P₂O₆) can be prepared by the slow oxidation of elemental P in the presence of water (146). It is normally prepared by the oxidation of finely divided red phosphorus with sodium chlorite at room temperature (145,146,151). The (-P-)₆ ring acid is formed by oxidizing red phosphorus, suspended in a solution of KOH, with potassium hypochlorite or bromine (151).

P-P-P anions are formed by oxidation of (-P-)₆ ring anions with iodine in a solution of potassium hydrogen carbonate (151). P-O-P-P acid and its salts are prepared by the oxidation of P-P-P-, P-O-P-P-, or (-P-)₆ ring salts with bromine in a solution of potassium hydrogen carbonate. The typical yields are 70, 50 or 20 % respectively (151).

In general terms, the synthesis of P-P bond containing compounds is relatively difficult and only small-scale production methods have been reported. This factor, in addition to the susceptibility of the P-P bond to cleavage by different compounds (water, alcohols, halogens, halogen halides, etc.) has made the P-P bond containing compounds a chemical curiosity without important practical applications. For that reason, the introduction of a possible new source of these compounds using an easy reaction (as described later on in this Chapter) and the use of this product in polymers with excellent properties would be very important in the P-P
chemistry. However, a lot of analytical work (out of the scope of this thesis) is required to confirm the existence of the P-P bond in the obtained product described in the following section of this Chapter.

E-Phosphorus Chemistry in this Research

In this work we have concentrated primarily in exploring new synthesis reactions. Analysis and characterization of the resulting intermediate and final products is only now beginning. Consequently very little has been proven about the chemical structures of the new polymers and pre-polymers produced. This is not unusual in the field of phosphorus chemistry, where the structures of reaction products are not always clearly defined. One of the commonly used reactions in our prepolymer systems is (See Chapter VI):

\[
2 \ H_3PO_4 \ + \ 1 \ Oxalic \ acid \ \longrightarrow \ A \ + \ CO_2 \\
T \ 110 \, ^oC
\]

The compound A is then reacted with two moles of ethylene glycol and the final product has been used in several formulations in this research. Also, several other stoichiometric combinations of H$_3$PO$_4$ and Oxalic acid (1/1, 2/1, 3/2, etc.) have been used but the resulting product is always "similar" to the product A.

The generation of CO$_2$ during the reaction was qualitatively proved by bubbling the generated gases into a solution of lead acetate (10%, wt.),
generating a white precipitate which is characteristic reaction of CO₂ (152).

Gas chromatography - Mass spectroscopy (GC-MS) techniques have been used to identify the structure of the product A, showing that it corresponds to a mixture of products. The most important products have MW 284 and MW 205 (See results in Figures VIII-3 to VIII-5). The same products are formed when the stoichiometric relation H₃PO₄/Oxalic acid is changed from 2/1 to 1/1, to 3/2, etc.

Several structures can be proposed for these MW, some of them including the P-P bond, as follows:

![Diagram of molecular structures with MW 205 and 284 showing P-P bonds and various oxygen bonds.](image-url)
FIGURE VIII-3  GC-MS RESULTS: 2 MOLE \( \text{H}_3\text{PO}_4 \)/1 mole oxalic acid.
FIGURE VIII-4 GC-MS RESULTS: 3 moles H₃PO₄/2 moles oxalic acid.
FIGURE VIII-5 GC-MS RESULTS: 1 moles $\text{H}_3\text{PO}_4$/1 moles oxalic acid.
IX- SUGGESTIONS FOR FUTURE WORK

A- Synthesis Project

In the short time of this research project we have generated a tremendous variety of nonflammable formulations (166 different foams), with a wide range of properties (advantages and disadvantages). Consequently a systematic effort to identify, investigate and optimize the most promising structures will be necessary at this point. Obviously the properties to aim for are ease of foaming, flexibility, and chemical stability of the resulting products.
Specifically, the following tasks are recommended:

1) The LOI for several of these foams should be tested, trying to get better information as to which formulations are the most nonflammable. It is recommended to reduce the final number of formulations to 3 or 4 which combine the highest LOI with best TGA, stability and flexibility. These formulations should then be further optimized by further structural modifications in order to get still better results. A preliminary selection (based basically on qualitative data) was made in this work and for that reason only a few formulations were reported in Chapter VI.

2) Additional flexibility can be introduced into these foams by combining structures based on s-triazines with perfluoroether chains, either as ligands or pendant groups. As can be seen from system P-100 and other results obtained at Rice University (both during a previous project and at the start
of this work), the combination of F-containing products especially with the pre-polymers based on s-triazines yields polymers with excellent stability, nonflammability and flexibility. The one serious drawback of this approach is a dramatic increase in cost since the perfluoroether reagents cost about $1 per gram, compared to $1-10/Kg of the reagents used in the other systems investigated in this project.

3) For commercial applications some of the foaming reactions should be accelerated. The proposed approach (which has been successfully tried out in this work) is to prepare two precursors: one of them acid and another alkaline, so the neutralization heat helps to accelerate the crosslinking. In order to keep high contents of P and N in the polymers, the acidity can be increased incorporating H$_3$PO$_4$ and the alkalinity by incorporating hydrazine, MEA, DEA, etc.

4) Some of the nonflammable foams (Foams 375, 549 and 513, described in Chapter VI) melt at relatively low temperatures (near 200 oC). So, they must be re-formulated in order to get increased cross-linking.

5) Similarly, according to the TGA (see Chapter VII) some foams (like BL-1, 510), lose weight at low temperatures (between 150 and 300 oC) although they keep between 30 and 40% of their weight at temperatures as high as 800 oC (under N$_2$ flow). These "premature" weight losses are attributed even to losses of water or losses of un-reacted hydroxyl groups. A determination of the gases evolved is required in order to evaluate the possible advantages-disadvantages of this characteristic. If it is due to water losses, it may be a significant advantage in fire protection, since the release
of water is endothermic and steam is a fire suppressant. If it is due to losses of hydroxyl groups the recommendation would be to try to react these groups with metals. Addition of CaCO₃, ATH, etc., with this purpose would be a first approach.

6) Finally is convenient to include some suggestions for improving the laboratory equipment used, as follows:
   a) It's necessary to implement a more homogeneous and controllable way for heating the prepolymers during the foam production. The HTS bath and the oven used in this work don't meet the requirements.
   b) For the case of instantly foaming systems (case in which only pre-heating of the pre-polymers is required), a new system for vigorous mixing is necessary in order to obtain certain degree of homogeneity in spite of the fast cross-linking. Of course, another possibility would be to slow down the foaming process by adjustment of the pH* of each of the components.

B- Analytical Work

This research has been centered on the synthesis of new polymers but the exact chemistry of many reactions has not been proved. So, an obvious step (at least from the scientific point of view) would be to use some analytical techniques (GC-MS, IR, NMR, etc.) to try to identify the products of many un-reported reactions used in this research. Initially, analytical work should be done in two main fields:

* These instantly foaming systems are based in two components, one of them acid and the other alkaline. The neutralization heat helps the crosslinking process.
1) Identification of the reaction product of $\text{H}_3\text{PO}_4$ and oxalic acid (in different stoichiometric relationships), as described in Chapters VI and VIII.

2) Identification of the structures of the pre-polymers and polymers obtained with the procedures described in Chapter VI.

**C- Physical Properties - Measurement**

After selecting the best foaming systems, a good measure of some physical properties (flexibility, stress-strain behavior, cell type, cell size, thermal resistivity for rigid foams, etc.) should be made. The literature (8) explains the commercially used methods but, as stated before, these were not used in this research due to the tremendous quantity of samples.

**D- Improvement in Foam Quality**

Although some of the obtained foams (produced without additives and with simple laboratory equipment) exhibit homogeneities and cell sizes very similar to commercial products, in general the quality of the obtained foams can be substantially improved by additives and modifications of the foaming process. The main suggestions regarding these topics are:

1) Additives
a) Use surfactants for improving the physical properties (cell size, homogeneity, etc.) of the foams. This suggestion is valid for most of the foams produced in this work.
b) Other additives such as mold release agents, coloring materials (for a better appearance), etc could be used for getting still better materials. In some cases metallic Aluminum has been used in this research. This material not only improves the nonflammability but also confers a silver color to the foams.

2) Foaming Systems

As stated in the Introduction, the development of foaming systems which could be used in the existing foaming machines would be an excellent advantage. To obtain this characteristic the main conditions would be:
a) Convert all the selected foaming systems (see Chapter VI) into two-component systems which should react easily when mixed properly.
b) Keep the viscosity of both components in a range similar to the viscosities of polyols and isocyanates. If one of the components is solid (at room temperature), it should have low melting point. In some cases these characteristics can be achieved by correct selection of the prepolymer to be mixed in order to convert the foaming systems into two-component systems. In other cases some reformulations could be required.

E- Use of Alternative Chemistry to Synthesize Other Polymeric Materials

In addition to foam systems, a promising variety of new nonflammable and thermally stable polymers, with many different applications, could be
developed, based on the alternative chemistry guidelines used in this research. Besides that, other non polymeric products, such as nonflammable lubricants, heat transfer fluids, plasticizers, etc. could be also developed with some improvements to the prepolymer and other intermediate products obtained in this work.

In general, the incorporation of inorganic elements in macromolecules can generate a lot of new properties regarding nonflammability, thermal stability, electrical conductivity (for electrical conductors and semiconductors), crystallizability, mechanical strength, controlled sensitivity to hydrolysis (for medical applications), etc. In fact, there are unlimited possibilities for inorganic or partially inorganic polymers, because practically all the polymer chemistry has concentrated in carbon, but there are several other elements (being P and N one of the most promising) that could yield properties which cannot be obtained with organic polymers.
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