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# Plastics Flammability

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# Plastics Flammability

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**Plastics flammability is discussed in relation to materials, chemical mechanisms, and the meaning and relevance of the term "flame retardant". Detailed discussion and tables of materials are presented in relation to oxygen indices and these are interpreted on the basis of structure-property relationships.** 

## **INTRODUCTION**

Given sufficient oxygen and heat, all organic polymers burn. All organic polymers evolve toxic products of combustion when burned, if only carbon monoxide. Absolute fire safety of organic polymeric materials does not exist. Yet millions of metric tons of synthetic (plastics) and natural (wood and wool) polymers are used annually in the United States without presenting an unmanageable fire safety problem. It is, however, argued that *some* applications of synthetic polymers *may* have augmented fire hazards in certain applications.

Most synthetic organic polymers (plastics) burn in a manner different from that of the most familiar of natural polymers-the cellulosics--wood, paper and cotton. Some synthetics burn faster, some slower; some give off more smoke, some less, some under different conditions; a few evolve more toxic gases, some less; and some melt and flow when subjected to heat while others char over extensively. However, the general magnitude of combustibility is of the same order for both synthetic and natural organic polymers. Both burn yet both can be used safely without undue risk.

In this paper we will discuss the flammability of organic polymers: materials, chemical mechanisms, and the meaning and relevance of the term "flame retardant".



**13. Filter** 

**FIGURE 1 Oxygen index apparatus (ASTM D2863).** 

If we were starting today from a zero data base, what could we learn in a few months about the flammability aspects of organic materials? Let's approach the topic from that assumption.

## **IN THE BEGINNING**

One of the tests which has been of considerable value in flammability research is the Oxygen Index Test (ASTM **D2863)** (Figure 1). For our exploration of organic materials let's use that test method. In the beginning of fire research let us assume that there was the Oxygen Index. Oxygen Index is a measure of ease of extinction. A material is placed in the center of a glass cylinder. At the base of the cylinder air is fed in which the percentage of oxygen can be varied. A small gas flame is applied to the top of the sample until the sample is well lit. If sustained combustion occurs after ignition, the test is repeated at a lower oxygen concentration in the test air until an atmosphere is reached which will not sustain continued combustion of the sample. The oxygen index of a specimen is the minimum percentage of oxygen in an oxygen/nitrogen atmosphere which will just sustain combustion of the specimen, i.e., the limit where the



## **OXYGEN INDEX VALUES FOR 600 FLUIDS AND POWDERS**

**FIGURE 2 Plot of oxygen index versus** number of **compounds at each oxygen index value for** *600* **fluids and powders.** 

sample would burn forever. For the test, sticks of polymer can be used, as well as powders, fluids and gases.

Having access to a good chemical stockroom, let us test some **600** different fluids and powders over several months. The results are shown in Figure **2. A** mean is observed at an oxygen index of **18** and the average for the 600 samples is an oxygen index of **20.** Clearly, with an oxygen percentage of **21** in air, most organics will readily undergo self-sustained combustion in air after ignition. The percentage of materials with oxygen indices well above **20** is small. We note with interest that all simple hydrocarbons whether pentane, hexane, or polyethylene or polypropylene are in the range of 15.5-1 7.5 (Table I). Even propane has an oxygen index of 15.5. Since the fuels are similar in each case and oxygen index is a measure of ease of extinction this should be expected. If we do the same with benzene and polyphenylenes, however, we find different behaviorsteadily increasing oxygen index as the number of aromatic rings **is** increased (Table I).

| Oxygen indices of polyphenyls    |      |  |
|----------------------------------|------|--|
| Compounds                        | ΟI   |  |
| Benzene                          | 16.3 |  |
| Biphenyl                         | 17.7 |  |
| p-Terphenyl                      | 18.6 |  |
| Quaterphenyl                     | 26.0 |  |
| Polyphenyl                       | 32.0 |  |
| Oxygen indices of polymethylenes |      |  |
| Pentane                          | 15.6 |  |
| Hexane                           | 15.5 |  |
| Cyclohexane                      | 16.3 |  |
| Decane                           | 16.0 |  |
| Hexadecane                       | 15.5 |  |
| Mineral oil (USP)                | 16.1 |  |
| Paraffin oil (heavy)             | 16.4 |  |
| Paraffin wax                     | 17.3 |  |
| Polyethylene                     | 17.4 |  |
| Polypropylene                    | 17.4 |  |

**TABLE 1 Oxygen indices of polyphenyls** 

If we examine 100 representative compounds (Table 11) we note the following: most organic functional groups have little effect on flammability. It matters little from a flammability standpoint whether we have an amine, ketone, carboxylic ester, carboxylic acid or alcohol. The first sixty compounds of Table I1 are all of oxygen index 19 or lower. **As** we move into the next **20**  compounds, however, we notice a predominance of phosphorus compounds and a few halogen substituted aromatics. We also notice Number **80,** phenolphthalein, which is a multi-nuclear aromatic. Of the final **20** compounds, **13** 

## **PLASTICS FLAMMABILITY**

## TABLE **I1**

Oxygen indices of 100 fluids and powders



are halogen containing materials and two contain phosphorus. Sucrose is present which chars readily (No. **82)** as is graphite powder (No. 99).

Qualitatively from this data we would have learned the following:

**1)** Most organic functionality has little effect on flammability.

**2)** Halogen and phosphorus compounds exhibit flame retardant properties.

3) Aromatic chains are intrinsically flame retardant and can be made further flame retardant by the addition of electron withdrawing substituents and by multi-substitution.

**4)** Materials which char readily are useful from a flammability standpoint

If we do a detailed analysis (Figure **3A)** of chlorinated aromatics we find a quite regular relationship between chlorine content and oxygen index. Superimposed on this relationship we find the effect of increased aromaticity



**FIGURE 3A Plot of oxygen index versus percent chlorine** for **polychlorinated biphenyls..** 

(Figure 3B) on going from one-phenyl to two-phenyl to three-phenyl rings If aliphatic groups are added (Figure **3C)** the effect observed is dilution of the chlorine content and a resulting reduction in oxygen index. For aliphatic halogen compounds we also see a regular relationship between oxygen index and halogen content (Figure **4).** From such plots the relative effectiveness of halogen is ascertained as shown in Table **111.** Halogens are more effective in aromatics than aliphatics. Bromine is twice as effective as chlorine with iodine comparable to bromine.

By such investigations many of the detailed organic chemical structure/ flammability relationships would have been elucidated. In Table **IV** are given oxygen indices for various synthetic polymers. Most of those polymers with oxygen indices above 21 are either halogen containing or have aromatic backbone chains.



FIGURE 3B Plot of oxygen index versus percent chlorine for chlorobenzenes, chlorobiphenyls, and chloroterphenyls.



FIGURE 3C Data for chloroxylenes superimposed over plot of oxygen index versus percent chlorine for chlorobenzenes, chlorobiphenyls and chloroterphenyls.





**a** Based on units of approximately sixcarbons.

#### TABLE IV

Oxygen indices of various plastics



## **FLAME RETARDANT POLYMERS**

Flame retardant materials can be discussed in terms of two basic groups, largely on the basis of cost. On the one hand there are those less expensive materials derived from commodity high volume plastics through incorporation of additives or by the introduction of flame retardant moieties into the backbone of the polymer. On the other hand, there are the more expensive intrinsically flame retardant, high temperature aromatic materials.

**A** number of basic types of simple flame retardant additives are in commercial use today. In approximate order of volume importance (including PVC plasticizers) are phosphorus containing materials and halogen containing materials, followed by combinations of halogen materials with antimony oxide. In addition, certain nitrogen and boron compounds as well as



FIGURE 4 Plot of oxygen index as a function of chain length for 1-halo and  $a, \omega$ -dibromoalkanes.

TABLE V

Average percentage requirements of additives to render polymers of minimal fire retardance using halogen or halogen plus antimony oxide



alkali metal salts and hydrates of metal oxides have found use in specific systems. It should be emphasized that commercial flame retardant materials are finely tuned systems including not only resin and flame retardants, but also

fillers, antioxidants, processing aids, pigments, stabilizers, and plasticizers. The whole system must be optimized with respect to a variety of properties including processability, long life, and cost such that the final material will fill a niche in the spectrum of available materials. Choosing the proper system is necessarily a trade-off of many factors. Not all flame retardants function in all plastics. Some are more effective in particular systems than in others. In Table V is presented average halogen requirements for various polymers as well as antimony oxide/halogen requirements to obtain a minimally flame retardant product. Large amounts of flame retardant are sometimes necessary. The major problem encountered, however, is not finding flame retardant systems for a given polymer, but the retention of acceptable physical and mechanical properties in a final product.

While theadditive approach may be simple, incorporation of flame retardant units into the polymer backbone may be more effective for the overall desired product. The main advantage of incorporating flame retardant monomeric units into the backbone of a polymer are: (a) the permanence of the flame retardant moiety in the polymer-no leaching or migration and (b) maintenance of physical properties of the polymer system. In some cases properties have even been improved by incorporation of flame retardant monomers. Unfortunately, incorporating flame retardant monomers into the polymer backbone is usually more costly than using additives because of the additional process expense. There are a rather large number of flame retardant monomers (examples shown in Table VI). New flame retardant monomers are continually being introduced as the need for flame retardant polymer systems increases.

The second category of flame retardant materials is that of high temperature polymers. **As** more stringent properties are required, more flame retardant products are utilizing these special materials. The topic of high temperature polymers is rather broad. For our purposes it encompasses two types of polymers: (a) those suitable for use at extreme temperatures for a few minutes (600-1000°C) and (b) those that function at moderate temperatures of **200-**  3000°C in air for long periods of time. Historically both areas have been studied extensively. In the **1950s,** considerable work was done to develop ablative heat shield materials for re-entry vehicles where surface temperatures briefly reach several thousand degrees Celsius. Phenolic resins were found to be ideally suited for use as the material in these shields because of their high char yield and nonmelting character. **Work** was **also** carried out to develop resins which possessed long-term use temperatures in the 200-300°C range. In the early **1960s** this work resulted in the commercial availability of a family of aromatic polyamides with excellent temperature stability up to 300°C.

Because of concern for flame retardant plastics substantial effort continues today in the area of high temperature polymers. New flame retardant materials are being developed which resist burning **or** melting on exposure to fire stress.

#### **TABLE VI**





To prepare polymers of high thermal stability three approaches have been used: (a) The preparation of linear single strand polymers based on aromatic systems, i.e., linear aromatic polyesters and polyamides; (b) The preparation of "ladder" polymers where the structure is bonded together in an uninterrupted sequence of cyclic structures (either aliphatic, aromatic, or heterocyclic); and (c) The synthesis of spiro polymers in which one carbon is common to two rings. Figure 5 shows the types of structures generated by these approaches.

In general, the premise behind all three approaches is that polymers having more aromatic character and very strong connecting linkages between rings will, upon heating, produce residues retaining more of the carbon of the original polymer. A good example of this is polyphenylene. This material is a crystalline, high melting substance which is very insoluble in all solvents. The thermal degradation begins in the **5W600"C** range and goes up to 900°C with only 20-30 per cent weight loss. As expected, introducing methyl groups either as substituents or methylene groups between the phenyl rings improves the tractability of these systems but diminishes their thermal stability. The use of



**FIGURE** *5* **Illustration of the types of high temperature polymers.** 

various combinations of atoms and groups linked with  $p$ -phenylene units is shown in Table **VII.** Such groups are found in various commercial high temperature polymers. Commercial materials in this category include poly- (2,6-dimethylphenylene oxide) **(PPOB), bisphenol-A-polycarbonate,** polyamides, polyethersulfones, and aromatic polyesters. **As** one goes to ladder and spiro polymers one reaches quite expensive specialty materials.

## **CHEMISTRY OF FLAME RETARDANCY**

**A** good deal is known about the chemistry of flame retardancy in polymeric materials. When a polymeric material is subjected to heat it undergoes decomposition producing volatile polymer fragments at the polymer surface (Figure 6). The role of molecular oxygen in this surface decomposition depends upon the specific polymer. The fuel thus produced diffuses to the flame front where it is oxydized producing heat which in turn causes more material decomposition. **A** cyclic process is established. Solid material is decomposed producing fuel which burns giving heat which results in more material decomposition. To decrease the ability of a material to burn, this cycle must be

#### **TABLE VII**

**Common p-phenylene linkages used in high temperature polymers** 



attacked in either the vapor phase or at the solid material surface. Vapor phase inhibition is achieved by additives which when volatilized disrupt the flame chemistry. Vapor phase inhibition is commonly achieved with bromocompounds and chlorocompounds with antimony oxide. Polystyrene and **ABS** materials use this approach. Solid phase inhibition may be achieved by the addition of species which promote the retention of fuel as carbonaceous char providing a protective insulating layer preventing further fuel evolution and otherwise altering the chemistry of the solid surface. Such an approach is effective in polycarbonate and in modified PPO<sup>®</sup> resins. Other solid phase approaches involve the use of heat sinks such as hydrated alumina or altering the decomposition chemistry to consume additional heat in the decomposition process. The specific functionality and modes of retardancy for flame retardant additives are outlined as follows. It should be noted that many of these statements could be described as "best guesses".



**FIGURE 6 The flammability cycle: when a polymeric material is subjected to heat it undergoes decomposition producing volatile polymer fragments at the polymer surface. The fuel thus produced diffuses to the flame front there producing heat which in turn causes more material decomposition.** 

## **Phosphorus additives**

(a) The thermolysis of phosphorus materials yields phosphorous acids and anhydrides which promote dehydration leading to water vapor and promotion of carbonaceous char. (b) Reaction cooling is accomplished by the endothermic reduction of phosphorus species by carbon. (c) Formation of a stable, glassy, protective mask of polymetaphosphoric acid is considered a mode of action for phosphorus fire retardants. (d) Phosphorus materials have also shown effectiveness as vapor phase inhibitors.

## **Halogen additives**

(a) Halogens show activity in quenching the chain-carrying free radicals present in the burning flame. (b) In the solid state decomposition zone, halogen acids catalyze solid char formation (particularly of polyolefins).

## **Phosphorus-halogen systems**

(a) Phosphorus halides and oxyhalides are flame free-radical quenchers and are more active than the halogen acids alone. (b) When a single chemical moiety contains both halogen and phosphorus, the relative ease of breakdown of the phosphorus compound enhances the availability of halogen species.

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## **Antimony-halogen systems**

(a) **A** chain of reactions leading to antimony halides and oxyhalides provides free-radical quenching effectiveness even higher than those of phosphorus analogs or halogens. (b) The end product of the reactions occurring when antimony and halogen are present in the combustion zone is thought to be solid antimony oxide in a finely divided form. Injecting fine particles into the reaction zone is known to reduce flame propagation rates. (c) Solid state catalysis directs formation of highly stable, intumescent, carbonaceous chars.

## **Phosphorus-nitrogen systems**

When present, phosphorus-nitrogen interaction can alter the course of thermal decomposition to enhance char development. Not all polymeric media display responses to phosphorus-nitrogen interaction, but composites of plastics with cellulosic materials often show strong positive responses.

## **Inorganic materials**

**A** number of filler materials of mineral origin contribute volume, structure, and thermal stability to carbonaceous chars once promoted by other routes. Vaporization of water of hydration in some cases may be inferred, as well as the catalysis of dehydrochlorination reactions.

## **SO IT'S FLAME RETARDANT?**

If we were to stop here one might make the assumption that we have a lot of "flame retardant" materials, that they are all equal, and that they are all "safe". Flame retardancy is, however, determined by standard laboratory tests. These tests measure one or more of the following properties: ease of ignition, flame spread, fire endurance, rate of heat release, ease of extinction, smoke, and products of combustion. No standard laboratory test measures all of these properties, therefore the reader should beware of being misled by the term "flame retardant" if it is not specifically referenced to a standard test. Indeed, the application of the term flame retardant comes from the fact that materials have passed one or more specific flammability test standards and that these materials perform better than a similar untreated material or other material used in the same application. Flame retardant and noncombustible are not synonymous. Flame retardant is not an absolute. The translation of "flame retardant" to "fire safe" requires analysis, judgment, and opinion of what constitutes reasonable risk in a particular end use. The degree **of** risk is not zero. In addition what value that risk takes depends not only upon the material

used but upon the total system (including people) and the severity of the expected stress. Such comments would not be unexpected for discussions of mechanical or physical properties of materials and should not be unexpected for material flammability behavior.

Data frequently available on materials are from small bunsen burner tests. Many of the common bunsen burner tests measure only ignitability : ASTM D635, **UL** Standard **94,** and FAR 25.853. Ignitability is important yet it is not the sole measure of flammability. For example, Radiant Panel (ASTM E162) flame spread indices (I<sub>s</sub>) as obtained for UL Standard 94 V-O structural foam samples show over an order of magnitude spread in results (Table **VIII); V-0**  flame retardant polycarbonate shows much better flame spread characteristics than **V-0** flame retardant polystyrene. While **all** these materials are difficult to ignite they show considerable difference in flame spread characteristics.

We need to exercise care in understanding what the addition of flame retardant additives has meant to the fire performance of a material and the meaning of the specific tests used. Discussions of flame retardancy are really meaningless without test data on performance. Have we improved ignition resistance/or flame spread characteristics/or the fire endurance of the material/or the rate of heat release/or reduced the smoke/or the toxic products of combustion? In the end, all organic polymers burn. Fire safety is involved with preventing ignition by likely ignition sources, lengthening time to involvement and penetration if fire occurs, and reducing fire impact; thus preventing most fires, increasing escape time and reducing property damage for those that do occur.

In the end, then, the suitability of particular classes of materials must be demonstrated in test simulations akin to actual fire conditions. For example, in order to evaluate the fire performance of materials used in systems, we at General Electric Plastics Division have had an extensive program of largescale fire tests designed to provide supplemental information to that of standard laboratory tests. Some **450** large-scale fire tests have been conducted from evaluation of window glazing to covered walkways, to mock-ups of bus

| Material         | Average $l_s$ |
|------------------|---------------|
| FR-polycarbonate | 18            |
| FR-PBT           | 23            |
| Polycarbonate    | 79            |
| Red oak          | 100           |
| Modified PPO     | 110           |
| Hardboard        | 152           |
| FR-polystyrene   | 240           |

**TABLE VIII Average radiant panel test results (V-0 materials) for &-inch structural foam samples** 

interiors. The fire test facility **is** shown in Figure **7.** It consists of a **12** by 14 foot test room lined with gypsum wallboard, not unlike a room in a typical home or office. Considerable instrumentation yields temperature, gas, and smoke profiles in the room versus time during the course of the test fire. The test instruments are housed in an adjacent mobile analytical laboratory. Data developed in the test are monitored by use of a computerized digital data logging system.

While large-scale fire tests are perhaps more representative of potential material performance than small- **or** medium-scale laboratory tests, since actual fire conditions may vary considerably, even large-scale tests themselves may not always fully predict material performance. Yet it is clear that provision must be made for large-scale fire test data such as room tests or window tests in the evaluation process to insure that materials with improved fire performance are really improved rather than artifacts of a particular laboratory test. The closer the test is to the actual application, the more confidence that can be placed in the result.

While we hope that large-scale tests will correlate with laboratory tests such is not always the case. The complexity of fire test results will continue to plague and challenge research workers in their establishment of research goals. **As** a result of the data at present it is clear that large-scale testing or



**FIGURE 7 General Electric Plastics Division Fire Test Center at Mt. Vernon, Indiana. The Center includes a fire test room, center right; a mobile analytical laboratory, left; and a storage building. Since real fire behavior is sensitive to weather, a weather station is included as part of the instrumentation.** 

assembly testing must play a far more important role than in the past in determinations of material fire performance and in research on flame retardant materials. Recognizing this, we at General Electric are continuing our emphasis on large-scale fire tests in research into new flame retardant products.

Of course, fire prevention and management involves not only the use of appropriate flame retardant materials but education, codes and standards, engineering design, fire detection systems, and automatic suppression systems.

## **CONCLUSION**

Flame retardant polymers is a topic of broad significance. In the foregoing pages we have attempted to provide an overview on flame retardant materials and their chemistry. **As** fires continue, pressures on materials will (rightly or wrongly) increase. Judgments on materials have to be made under the pressure of gravity and complexity of the problems to be solved, and frequently on the basis **of** inadequate data. The authorities expect, the press demands, and many manufacturers promise "safety" from injury to health through new materials. Legislators use the term "harmlessness" in laws and regulations. Both safety and harmlessness imply a guarantee and inevitably persuade the layman that such protection can, in fact, be given no matter what is done with a given material. Unfortunately, scientific experiments are fundamentally incapable of providing such a guarantee.

Tests can measure only relative safety, which must be defined according to the prevailing fund of scientific knowledge. Laymen must learn something about biological variability and quantitative relationships and they must realize that the use of materials, whether natural or synthetic, flame retardant or non-flame retardant, is fundamentally inseparable from risk. Yet it is also clear that synthetic organic polymers (plastics), with proper use and design, *can* be used safely without undue risk.

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