FOREIGN TECHNOLOGY CONCERNING FIRE SAFETY ASPECTS OF POLYMERIC MATERIALS

2LT Gus G. Orphanides, CmlC

Task No. 4201113SH

October 1973

FOREIGN SCIENCE AND TECHNOLOGY CENTER
ARMY MATERIEL COMMAND
US ARMY

TABLE OF CONTENTS

Introduction

The combustion of organic polymeric materials presents serious fire, smoke, and toxic vapor hazards. The growing use of these materials in all segments of our society has resulted in a heightened concern for the safety of human life and property. Scientific and technological solutions to the problem rest on improving present fire, smoke, and toxic vapor testing methods. This coupled with a fuller understanding of the dynamics of burning will lead to the development of organic materials that, as a result of composition and design, pose fewer and less severe combustion hazards. At this time, the technically advanced nations do not possess the necessary technology to accomplish this end. Nevertheless, these same countries realize the situation, and are striving to remedy it.

This paper presents the salient features of the foreign technology concerned with fire safety aspects of polymeric materials. It describes the current state of foreign test methods, of foreign contributions to the understanding of fire dynamics, and of foreign organic fire resistant polymers. Particular attention is paid to developments in the United Kingdom, France, West Germany, Japan, and the Soviet Union.

FIRE TEST METHODS

Background

Fire test methods are designed to provide information on the fire behavior of materials, and ideally are supposed to be a reliable basis for prediction of material behavior in an actual fire situation. Present foreign and domestic test methods have deficiencies which render them less than reliable in determining the fire properties of materials to define potential fire hazards. The inadequacies of fire test methods are many, and most technically advanced nations realize them and are attempting to develop new tests that exclude the shortcomings.

It is appropriate here to discuss some of the failings of present fire test methods. First of all, most tests were initially designed to be used for cellulosic materials, such as wood and cotton. With the advent of synthetic organic materials and their ever-expanding use in all phases of society, these tests are being employed for synthetics for which they may not be suitable. The design of the apparatus, the experimental conditions, and the criteria used for expressing results may need alteration from the original test specifications.

A second shortcoming is the reliance on small-scale laboratory testing to predict the behavior of a material in a full-scale fire situation. Small laboratory tests do not reproduce the massive heat effect of a full-scale fire, and thereby exclude a major factor that determines the spread of the fire, the damage to surrounding structures, and the hazard to life. A fire test should be designed with reference to a fire environment, and toward this end some large-scale test methods are being investigated by Canada and Great Britain. A test of the Canadian Standards Association is run on a final construction containing both the floor and ceiling assembly, while an American test, ASTM E-119, describes a large-scale wall test.

A further criticism is that when materials are tested alone but used in conjunction with other materials, the combined fire effect they have on one another is not measured in the performed test. A test not only has to reflect a real fire, but also must relate to an actual application of an item.

A fourth deficiency is the confusion and the contradictory nature of terms such as "flameproof", "self-extinguishing", "non-burning", and so on. At first glance these properties appear unequivocal. Yet, they can mean different things according to whether the tests are British, American, German, or Japanese. For example, confusion exists over "flammability", which is defined by British test BS 4422 as the capacity **of** a material to burn and defined by ASTM E176-66 as subject to easy ignition and rapid flaming combustion. The term "combustibility" also is surrounded by contradictions as illustrated by the results of a world-wide survey by H. W. Emmons (1). An international group submitted samples of 24 "combustible" materials to six European countries for rating by their national standard fire tests. Each county arranged the materials in order of combustibility. The lack of agreement is apparent when the results are examined (Table 1).

Table 1. Partial Listing of the Relative Rating of 24 Materials by Six Different National Standard Fire Rating Tests. The rating of 1 corresponds to most combustile, and 24 to least combustible. (1)

Material	W. Germany	Belgium	Denmark	France	Netherlands	UK
wood wool/cement slab	18	23.5	23	24	24	24
phenolic foam	24	23.5	1	21	19	19
expanded polystyrene	15	1	4	17	21	1
acrylic sheet	3	2	22	1	7	22

A fifth inadequacy of present fire test methods is the lack of reliable smoke tests and toxic vapor tests. There are some standardized smoke tests in West Germany, Netherlands, and the United States, but these methods define only a few conditions. Furthermore, there are no standard toxic vapor tests (under fire conditions) in the whole world. Tests have been proposed and carried out, however, that show toxic hazards of burning plastics on animals. The seriousness of the test inadequacies comes to light since the products of combustion, smoke, and toxic vapors appear to be the major causes of death in fires. This is supported by a study by Dr. A. W. Phillips (2) of the National Commission on Fire Prevention and Control (NCFPC). Phillips claims that 53% of victims succumbing in a fire die from inhaling smoke and harmful gases.

As was stated earlier, fire tests are designed to provide information on the fire behavior of materials. Fire behavior of polymeric materials can be characterized by six factors:

1. ignitability - or ease of ignition, defined as the ease with which a material is ignited under specificed conditions.
2. surface flame spread - defined as the rate of travel of a flame front under specific burning conditions. Some measures of flame spread are burning rate, flame spread factor, burning extent, and flame height.
3. fire resistance - defined as the resistance offered by the material to the passage of fire normal to the exposed surface over which the flame spread is measured.
4. heat release (fuel contribution) - defined as the heat produced by the combustion of a given weight of material.
5. smoke density - defined as the degree of light or sight obscuration produced by smoke from a burning material under given conditions.
6. toxic products - combustion products such as smoke and volatile gases.

Some of the foreign tests and standards that attempt to define the properties of organic materials are presented. Special attention is given to tests for smoke and toxic vapor production in subsequent sections.

United Kingdom

The Fire Research Station, the Greater London Council, and the UK Agreement Board are involved in fire tests and set appropriate standards for building materials. RAPRA (Rubber and Plastics Research Association) also has been investigating the relevance of present fire tests methods. All these organizations realize the deficiencies and are attempting to overcome them.

A recent fire in a cabaret on the Isle of Man brings the inadequacy of present fire test methods and standards into focus (3). The roof of the structure consisted of a plastic called ORGOGLASS whose fire properties made it unsuitable for such an application. The manufacturer indicated this in its information sheet. Nevertheless the material was used because the fire safety officer was not aware of its limitations. The point is that data on fire properties of materials are not easily accessible to those who need to have them. Although the Fire Research Station has tested over 4000 materials, these tests were paid for by the manufacturers and the results are not available to users. The same is true for the 300 tests performed by the Greater London Council. To circumvent this situation the British government set up the UK Agreement Board whose responsibility was to assess the performance of building materials and make the results public. However, use of the board by manufacturers, who by the way pay for the tests, is voluntary. Only 200 materials have so far been approved by this UK Board. The contrast should be drawn here between an analogous French Agreement Board which has approved over 4000 materials since 1963 for use in the building industry. Use of the French Board is obligatory and results are publicized. Consequently, critics argue that an easily accessible "handbook" is needed that clearly states the results of fire tests and describes the dangers and application restrictions of all new materials.

British Standard Test BS 476 consists of various parts, and in totality is used for evaluating building materials (4). BS 476 was revised in the past few years and has the following parts (5, 6):

Part 3. External Fire Exposure Roof Tests
Part 4. Non-combustibility Test for Materials
Part 5. Ignitability Test for Materials
Part 6. Fire Propagation Test for Materials
Part 7. Surface Spread of Flame Test for Materials
Part 8. Fire Resistance Tests for Elements of Building Construction
Part 9. (proposed) Smoke Density Test for Building Materials

The Ignitability Test for Materials (BS 476: Part 5) consists of applying a small flame to the surface of a vertically held sample. The test is similar to BS 4422: Part 2. Analogous foreign tests involve different orientations of the specimen and other heat sources. Consequently, comparative evaluations of ignitability show contradictions. The analogous American test for ignitability is ASTM D-1929.

The Fire Propagation Test (BS 476: Part 6) measures the heat contributed to the fire by the test material. It gives an indication of the pattern of heat evolution when a sample burns: (a) when exposed to a standard flame, and (b) when exposed to a standard flame and radiant heat. Materials are graded with respect to amount and rate of heat evolved, and an overall Fire Propagation Index is calculated by adding together three measured indices (7, 8).

- i_1, representing the early stages of ignition
- i_2, representing the growth to a fully developed fire
- i_3, representing the terminal stage of the fire

These indices are derived from measured temperature-time curves. Most foreign nations have similar tests, although they may differ in design details, and use a similar apparatus consisting of a "combustion box" provided with a controlled heat source. The British apparatus uses a multiple heat source and has an internal combustion chamber of 190mm x 190mm x 90mm (7).

BS 476: Part 7, the Surface Spread of Flame Test , has two versions (7). A preliminary (BS 476: Part 1) which is less severe, and the full scale which is the only version accepted by industry. In the full scale test the spread of flame is measured along a 300mm x 75 mm sample held in position at right angles to a 300mm, gas heated, square, radiant panel. The edge of the sample nearest to the panel is heated to 500°C. The test provides a means of assessing the tendency of a fire to spread through a building by travelling across the surfaces of combustible materials that have been preheated by radiation from the advancing fire. Four class ratings of materials are determined:

Class	Flame Spread at 1.5 min(cm)	Flame Spread at 10 min(cm)	Final Flame Spread(cm)
1	-	-	19
2	30	-	60
3	30	83	83
4	30	83	83

Building materials require class 1 or 2 ratings. Asbestos reinforced poly(vinyl chloride), and some glass-reinforced polyester and melamine laminates are rated class 1. In the United States, Underwriter's Laboratory Tunnel Test (ULE48) would give analogous ratings of 20 to 50 for class 1 materials.

BS 476: Part 7 and Part 6 complement one another when rating building materials and are appropriate for evaluating aircraft, land transport, and ship materials.

BS 476: Part 8 specifies fire resistance of building materials and structures and is similar to tests in other countries (8). In this test, full-size representative samples are exposed to standard heating conditions. The duration for which the criteria of stability, integrity, and insulation are satisfied is taken as the fire resistance of the specimen. International recommendation ISO R/834 also describes fire resistance testing for structures.

BS 476: Part 9 (Proposed) is a means of measuring smoke evolution in a fire (8). The test consists of performing the Fire Propagation Test (BS 476: Part 6) in a room of known volume equipped with two mixing fans of a specified air flow. The smoke density of flaming materials is calculated from observations of the obscuration of a light source across the center of the room. The percent obscuration (specific optical density) of the combustion products is then measured along with the rate of production.

Textile testing in the UK includes two standard methods BS 2963 and BS 4569 (revised in 1970) (9). The former is a vertical test method that is not suitable for napped fabrics. While the latter is an improved test in which the flame source is moved back and forth over the specimen to initiate ignition. BS 4569 is suitable for napped fabrics and is entitled "The Surface Flash in Pile Fabrics Test".

A combustibility test, BS 2782-508A, involves applying a flame for 10 seconds to a clamped specimen (9). The material is rated "self-extinguishing" if the burn does not reach 1 inch and the specimen burns for less than 5 seconds after flame removal. American test ASTM D-63572 is analogous except that the flame is applied for 30 seconds and the self-extinguishing ratings are different. According to the ASTM test if a specimen does not burn more than 3 seconds it is classed as "zero burning". If the burn does not exceed 4 inches then it is "self-extinguishing".

A Canadian standard put out by the Canadian Standards Association, designated CSA B54.3, defines fire tests for walls, partitions, floors, roofs, and ceilings (10).

An Australian standard that describes methods for fire tests on building materials and structures is designated by SAA A30 (10).

West Germany

In the Federal Republic of Germany many institutes are concerned with fire test methods for materials. Some of the facilities are: the Otto Graf Institute, Stuttgart; the Institute of Wood Research at the University of

Munich; the Research Station for Fire Protection at the University of Karlsruhe; the Federal Institute of Material Testing, Berlin; the Material Testing Council, Dortmund; and the Institute for Plastic Processing, Aachen. The last two facilities appear to be the key centers for research activities in test methods.

German industrial standard DIN 4102 is analogous to BS 476 in that they both define the fire test methods and classification of plastics and other building structures (7). The German standard consists of Parts 1 to 5, and classifies building materials according to combustibility. As of August 1972, complete specifications were not available for Parts 1 and 5. This German specification, however, includes testing of samples in a closed room (combustion shaft) at temperatures between 500-1000°C.

The testing of plastic floors is specified by DIN 51,961 and includes two tests (9). Test A involves placing a burning cigarette on a 100mm x 100mm sample and determining the time the plastic glows along a 40mm path. Test B measures changes and depth of burning after a burn time of 12 minutes when a cigarette is placed on a 200mm x 100mm specimen. Other building material tests are DIN 53,799, a test of laminated plastic slabs, and DIN 53,482 for testing the fire resistance of foils (7,9).

West Germany has standard tests for textiles as well (9). The "Test of the Burning Behavior of Textiles, Ideas and Applications" (DIN 54,330), which was in draft form in 1971, is claimed to represent an advancement in the establishment of unequivocal terms to define textile fire behavior properties, such as: noncombustible, hard to burn, combustible, easily burnable, after glow, ignitability, rate of flame propagation, and melting. The specification enphasizes the avoidance of confusing terms like "not-flammable" and "difficultly flammable".

German specification DIN 54,331, "The Determination of the Burning Behavior of Burnable Textiles, by the Arc-test Process", defines a test employing a burn box of 700mm x 390mm x 660 mm. The test measures burn-time, length of burn, and glow-period. The burn box for DIN 54,331 is also used in test specifications, such as:

DIN 53,906 - New Vertical Test Method

53,907 - New Horizontal Test Method

53,333 - The Flame Propagation Rate Test

54,334 - Ignition Time Test

54,332 - Test for the Combustibility of Textiles

Sweden

Combustibility tests are coordinated by the Swedish Institute for Building Research, Swedish Plastics Federation Division of Plastics in Building, and the Swedish Institute for Materiel Testing.

The Swedish "Hot-Box Test" (5, 9) is analogous to the British Fire Propagation Test (BS 476. Part 6). The Swedish test uses a single gas flame as heat source in a 300mm x 235mm x 235mm chamber. The rate and amount of heat evolution is measured from the obtained time-temperature curves. This "hot-box" is also used in a test for smoke density and rate of smoke evolution.

The Swedish Institute for Material Testing developed a test method for determining the combustibility of carpets under specification SP Br6 (9). A 40cm x 100cm sample is ignited in a tunnel with air velocity regulated at 2 meters per second. The test consists of determining the extent of damage along a 50cm long burn.

The Netherlands

The Fire Protection Center (TNO), in Delft, performs the fire tests of building materials (4). Chapter 3 of standard NEN 1076 describes combustibility tests and is similar to British Standard 476: Part 6, the Fire Propagation Test. The Dutch test is also characterized as the

"Flash Over Technique" in which two 300mm x 300mm specimens are exposed to radiating heat in such a way that they are separated by the heat source. One specimen is ignited by a gas flame, and the intensity of heat produced, that ignites the other sample, is measured.

Denmark

Danish fire standards are designated by DS notations and include:(1) DS 1057 defining fire classification of building of materials; (2) DS 1053, fire classification of doors; (3) DS 1052, fire classification of structures; and,(4)DS1051 describing fire resistance tests of structures (10).

Switzerland

A Swiss standard, SNV 198,898 which was in draft status in 1971, describes the determination of burn and glow periods of "difficultly combustible" textiles (9). The test is based on German standard DIN 53906 and American test AATCC-Test Method 34-1969. The Swiss test, however, does not include the effect of glass fibers on the fire properties, as do the German and American tests.

A testing apparatus, developed by the A. Hitz, Ahiba Company and designated FT70A, is claimed to be a versatile instrument in determining the flame propagation rates of textiles (9,11). The device allows specimens to be tested in specific positions, each varying with respect to the horizontal plane. According to the company, this advantageous feature may enable the apparatus to get international recognition and consequently may bring universal fire test methods for textiles a step closer to reality.

France

A French fire test developed by the Fire Safety Center measures an "ignition index", a "flame propagation index", a "maximum flame height index", and a "combustibility index". The test was modified in 1965 under designation 57-1161. The test involves exposing a 300mm x 400mm specimen to radiating heat. Building materials are categorized as follows:

Class 1 - incombustible, if the values of the igniting flame propagation and maximum flame height indices are zero.

Class 2 - hardly combustible, if the value of all indices is less than 1.

Class 3 - moderately combustible, if the ignition index is less than 2, and the combustion index is greater than 2.5

Class 4 - easily combustible, if none of the requirements of the first three classes can be met.

Japan

In Japan, the government has the authority to control industrial standards and uses the JIS-mark indication system. Japan is implementing international cooperation in establishing industrial standards. The Japanese are increasing their participation in the International Organization of Standards (ISO), and are attempting to make their JIS widely available to producers, distributors, users, and consumers of industrial products in Japan and in other countries (12).

Japan's growing concern with present fire test methods and standards is also apparent. In 1972, they expressed a desire to legislate non-flammable quality certification for all textiles and proposed a law setting safeguard fire standards in apartment houses and entertainment establishments (9).

The specification JIS L 1009-1966 describes three fire test methods for textiles (9). The standard is based on American test methods AATCC 33-1966 and AATCC 34-1969. Besides textile testing, a series of test methods exists for the determination of combustibility of building materials. Standard JIS K 5661 describes specifications of fire retardant paints for buildings (10).

USSR

In the Soviet Union, the Central Fire-Fighting Research Institute (ZNIIPO), in Moscow, is concerned with the problems of combustible materials. The amount of heat released during combustion is taken as a basis for classifying building materials as combustible. This differs from tests other countries use to determine combustibility. The test involves burning a 35mm x 75mm x 10mm specimen in a calorimeter. The quotient of the quantity of heat developing during burning and the quantity of heat delivered by the flame source is the "K value" and is the basis of classification. Ratings are based on the following "K values":

$K < 0.1$ - incombustible

$0.1 < K < 0.5$ - hardly combustible

$0.5 < K < 2.1$ - hardly flammable

$2.1 < K$ - easily flammable

Hungary

In Hungary, the fire behavior properties of building materials are investigated at the Fire Resistance Laboratory of the Institute for the Quality Control of Building. The Research Institute for the Plastics Industry and the Fire-Fighting Department of the Ministry of the Interior are also concerned with testing the combustibility of plastics.

The combustibility and fire resistance tests of building materials are specified by a series of standards designated MSz 14,800. Only 3 of the 12 proposed standards had been published as of 1972. These standards eventually will coordinate all test methods for building materials. Standard MSz 14,800/3 is based on the German standard DIN 4102 that defines combustibility.

Limited Oxygen Index Method

The Limited Oxygen Index Test, although initially developed at the General Electric Company, is receiving increased international recognition as a sensitive and reproducible technique for measuring a fundamental property of a material. The test (ASTM D2863-70) consists of adjusting the proportions of oxygen and nitrogen until a specimen burns for either a distance of 50mm or a time of 3 minutes (8). An Oxygen Index rating is determined, defining the lowest concentration of oxygen necessary for a material to burn under the above specifications. The test is small scale and may not always be relevant in describing the practical fire behavior of materials. The test, however, is used by the UK (8), Hungary (13), the USSR (14), Japan (15), and other European nations (16).

SMOKE TESTS

The toxicology of all fires consists of features, such as heat, oxygen deficiency, carbon monoxide and other gases, smoke,and panic or emotional shock. In the case of burning organic materials, however, the evolution of various toxic gases and dense smoke appears to be unique. Unfortunately less than reliable test methods exist for these products, despite the fact that they products present the greatest hazard to life in a real fire.

Smoke not only presents toxic hazards, but also can prevent escape from fires by obscuring vision. Smoke evolution in a fire is less reliably measured compared to heat release, ignitability, fire resistance, and flame spread (17, 18). There are a few American tests that attempt to define and measure smoke evolution (19). The Steiner Tunnel Test (ASTM E-84) is a large-scale test for smoke density. While small-scale tests include the Rohm and Haas XP-2 test (ASTM 2843- 70) and the National Bureau of Standards Smoke Chamber Test. The XP-2 test is claimed to correlate well with large-scale burning tests done outdoors. The NBS Smoke Chamber test employs a closed cabinet having a volume of 18 cubic feet. A 3-inch square specimen is exposed to heat under flaming or nonflaming conditions. Light absorption is measured vertically to minimize differences caused by stratification of the smoke. The test measures specific optical density, maximum smoke accumulation, maximum smoke accumulation rate, and time to reach maximum smoke density.

The ability of small-scale tests to predict smoke production in large fires was studied by the IIT Research Institute for the Society of the Plastics Industry in 1966 (19, 20). It was found that in the case of smoke hazards of interior finish materials, the data on smoke production are not adequately defined by a smoke rating number from a single small-scale test. The inadequacies appear to result from an inability to produce the extremely heavy smoke associated with total fires. Consequently, the study concluded that improved methods must be devised to predict smoke evolution. This assertion holds as true in 1973 as it did in 1966.

Foreign nations have recognized the problem and some of the technically advanced countries, such as the United Kingdom, the Netherlands, West Germany, and Switzerland, are conducting research to improve test methods to eventually lead to the control of smoke.

United Kingdom

In the United Kingdom, research at the Fire Research Station has led to the development of a smoke chamber measuring 3.6m x 3.36m x 2.79m (21). This chamber probably is the basis for Part 9 of BS 476 that was in "proposed" status in 1972. A schematic shows the apparatus (fig. 1).

British Smoke Chamber

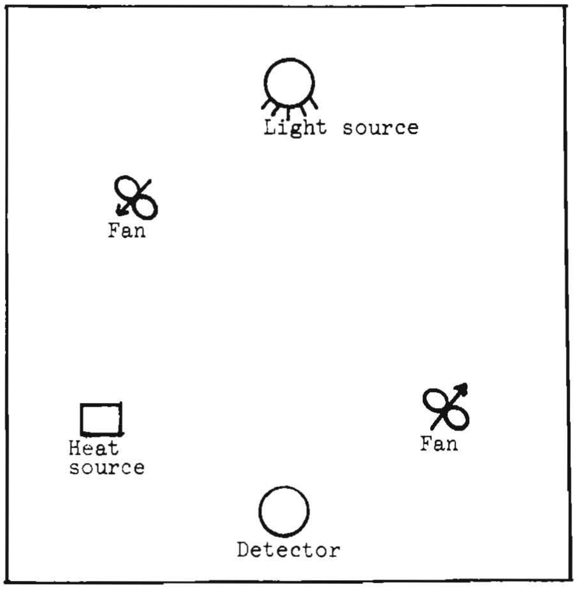

Figure 1

The test is designed to establish the smoke levels in escape corridors, which are adjacent to the room containing the burning material. Consequently, the test can predict the hazard that might prevent escape of persons from these adjoining rooms and corridors.

In February 1973, the Stanton Redcraft Company reported the marketing of an apparatus that they claim can effectively measure smoke and other flammability characteristics (22). The equipment consists of "Module FTA" (the critical oxygen index test apparatus) and "Module FTB"(the smoke density box). The firm claims the set-up can measure (1) flammability as expressed by the Critical Oxygen Index (COI), (2) smoke density, (3) temperature of burning, rate of burning, burning profile, after glow, and (4) formation and analysis of evolved gases. It appears that Stanton Redcraft has the proverbial "magic black box". Nevertheless, their claims have yet to be substantiated.

At the Queen Mary College conference on burning plastics in February 1973, British scientists reported that the scanning electron microscope (SEM) was useful in learning about smoke (23). In one example, smoke had been trapped in a water tank and examined on the surface of a grid showing it to consist of a carbon skeleton with crystalline inclusions. Although not reported yet, it is claimed that research into the char structure of flame retardant foams and other plastics might be possible by the use of the SEM.

The Netherlands

A Dutch smoke measurement apparatus is illustrated schematically (fig. 2) (21).

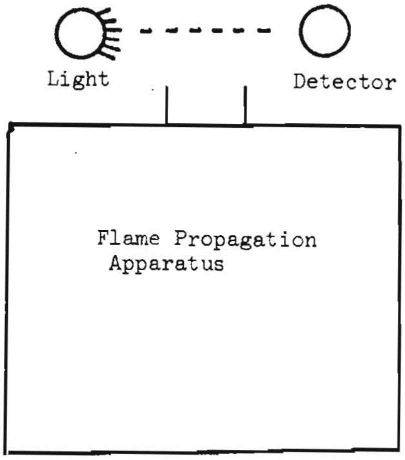

Figure 2.

The test is characterized by thermal decomposition from radiating heat. Smoke is liberated into the open air, and measurements are taken over the point of exit.

West Germany

German Standard DIN 53,436 (Draft as of 1972) describes an "Apparatus for the Thermal Decomposition of Plastics under Air Flow (5 liters/min)". The equipment is represented schematically (fig. 3) (21).

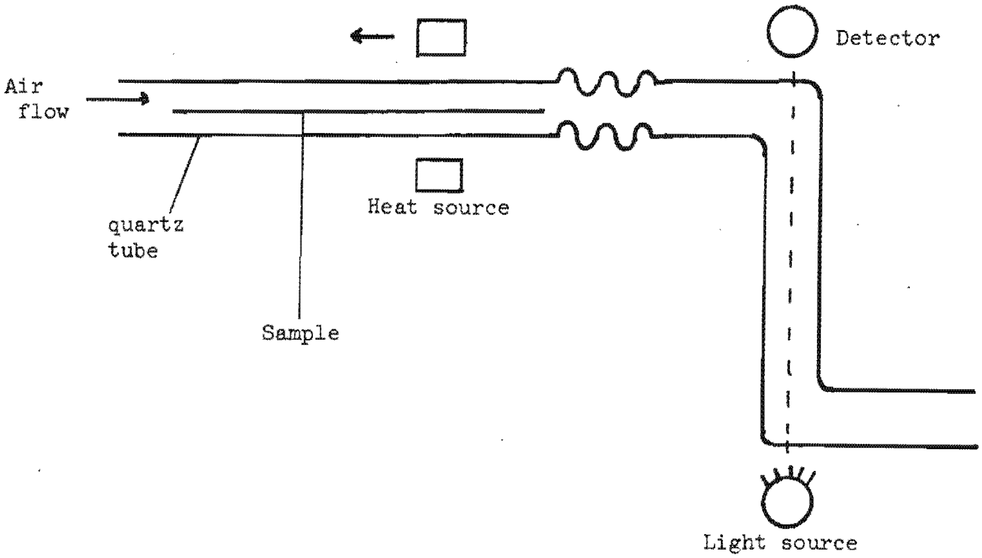

Figure 3.

The samples are burned in a 1 meter long quartz tube. The oven with a variable heat output is moved across the tube at 10 mm/minute, burning the material at a fixed rate. Air flow is maintained at 5 l/minute. Samples measure 1000mm x 15mm x 2mm.

In Switzerland and Sweden research also is underway in smoke density measurements. Nevertheless, there are no countries in the world that have a test that can reliably predict smoke generation under the myriad possible conditions associated with a real fire.

TOXIC GASES

In a fire, the type and amount of combustion products depend on the material, the temperature, the types of gases present, and the pressure conditions. Since organic materials are carbon compounds, carbon dioxide and carbon monoxide are the major products, depending on the availability of oxygen during burning. The presence of additives in plastics, such as stabilizers, fire retardants, and plasticizers, results in additional dangerous gases as well as harmful smoke production. The problem is most severe in the case of fires that occur in enclosed areas, such as inside ship and aircraft compartments. In such instances, escape routes become difficult to reach when dense smoke obscures vision. Furthermore, the lack of air flow prevents dispersion of the toxic products. One example of such a case is the recent crash killing 122 persons at Orly Airport, Paris (24). A fire consumed the interior of the plane before it landed. It is estimated that the fire was not propagated by fuel, but involved only material inside the craft. Large amounts of cyanide gas and carbon monoxide were present in the fire, and most deaths were attributed to these toxics rather than to the flames.

Presently, there are no standard tests to measure the toxic effects of combustion products. In some nations, however, there are tests that show toxicological effects, but none has received national or international recognition and approval. In the United States, there are even few fire code regulations covering toxic gases, and the knowledge of the subject is rather limited among fire fighters (19).

Reliable test methods for toxic products must include biological data and must show how life or life processes are affected in a real fire. In an actual fire situation, the toxic potential is the sum, either additive or synergistic, of all the various causes of death or incapacitation that are present.

In Canada, a technique has been developed for determining the "toxic potential" of materials (5). A known amount of a sample is decomposed at 900°C and the concentrations of poisonous gases are measured. These concentrations are related to the minimum lethal levels and are expressed as the toxicity potential. No synergistic effects are assumed in this test however.

American researchers, such as Boettner and Ball at the University of Michigan, Einhorn at the University of Utah, and Pryor at the Southwest Research Institute, San Antonio, also are actively pursuing the toxicological effects of combustion products from burning plastics (25).

In the United Kingdom, research at the Fire Research Station has involved the use of sophisticated spectrographic techniques to study the range of products from burning polymers (5). Researchers also intend to study the synergistic aspects of these products. According to H. L. Malhorta of the FRS, referring to the toxic vapor problem, "it is likely to be about five years before sufficient data become available to permit decisions to be taken on the likely hazards, methods of assessment, and methods of control."

Interesting work in this area is going on in West Germany (26). A proposed test defines conditions in which small specimens are decomposed at various temperatures. The toxicity of the combustion products then is determined by exposing mice to the resulting atmosphere. This test may be based on the work done by H. Oettel (26) of BASF (Badische-Anilin und Soda Fabrick), who determined the toxic effects of burning materials by measuring the percent of carbon monoxide-hemoglobin in the blood of exposed rats.

Effenberger (26) also has contributed to the solution of the problem. His work has involved exposing rats to the toxic environment of burning plastics. The apparatus described by DIN 53,436 (Draft) was attached to a plexiglas container into which the rats were placed. Five exhaust lines went into the tank. The time of exposure was 100 minutes. The criteria used to interpret the results were (1) comparison of the number of surviving rats to dead ones (Table 2), and (2) the content of carbon monoxide-hemoglobin in the blood(Table 3).

Table 2. Acute Death of Rats under the Influence of Combustion Products of Materials.

Material	Number of Rats	Number Dead	Number Unharmed
Pine wood	14	11	3
Wool fabric	9	0	9
Polystyrene	29	0	29
Laminated plastic	10	0	10
Melamine resin	17	2	15
Polyester cloth	9	0	9
Polyacrylonitrile	14	13	1
Polyurethane	20	2	18

Table 3. Average COHb - Content in the Blood of Rats Exposed to the Combustion Products of Materials.

Material	Number of Rats	Average COHb Content in the blood
Pine wood	11	66.1
Wool fabric	7	32.4
Polystyrene	7	3.2
Laminated plastic	6	42.7
Melamine resin	6	33.7
Polyester fabric	5	19.2
Polyacrylonitrile	8	3.0
Polyurethane foam	20	24.6

The results show that pine wood and polyacrylonitrile produced the greatest fatalities. Yet the carbon monoxide content in the blood of rats exposed to burning pine wood was twenty times that of the blood of rats exposed to burning polyacrylonitrile. In the latter case, hydrogen cyanide and ammonia gas are probably the major lethal gases.

Effenberger realized that these two tests did not take into account the more subtle effects of toxic gases. That is to say, the effect of the poisons in lowering mobility and thereby reducing the ability of the rats to try to escape. Therefore, he devised a "swimtest", which consisted of exposing rats to the combustion products of the same materials as before. Here, however, results were interpreted by determining the time each rat remained afloat and swimming before drowning (Table 4).

Table 4. Results of "Swim test".

Material	Number of Rats	Average Swim time (minutes)
Pine wood	7	4.0
Wool fabric	9	6.9
Polystyrene	23	1.3
Laminates	6	180.8
Melamine resins	8	84.2
Polyester fabric	14	79.0
Polyacrylonitrile	22	8.1
Polyurethane foam	11	55.3

The startling results show that burning polystyrene, which produced no dead rats in the other experiments and resulted in a very low carbon monoxide content, caused the shortest swim-time resulting in death by drowning. The unique burning product evolved, other than carbon monoxide, is styrene which apparently has an immobilizing effect on the rat. This interpretation may be extended to fires involving humans, in which death may be imminent because the ability to escape from the fire is impaired.

In Japan, work done at the University of Tokyo, in 1971, also involved exposing mice to the toxic environment of burning materials (27). Exposure time was 15 minutes and pyrolysis temperatures were near 790°C. Results were interpreted by comparing mortality rates due to exposure to the respective burning samples.

With the increased use of organic materials has come a growing awareness in the toxicology of combustion products. Unfortunately, standardized tests that involve biological evaluation of degradation products are not available at present, although tests do exist. The problem is realized in the technically advanced nations, and test procedures have been proposed for standardization in some of these countries.

DYNAMICS OF FIRE

Current Theory

The study of the burning processes of materials is geared to a better understanding of dynamic aspects, such as ignition, flame propagation (or spread), and thermal decomposition, so that new materials may be developed that, as a result of composition and design, will have reduced fire hazards. A review by Einhorn (25), at the University of Utah, presents a detailed picture of the mechanism of combustion of materials. A brief summary is presented here, and some of the contributions of foreign scientists to the study of flame propagation follows.

According to Einhorn, a material burns in several stages (fig. 4). An external heat source (flaming, non-flaming, or electrical) is applied to a material. This source may also introduce free-radical species and cause the material to react further by liberating gases or combining with oxygen. These two processes increase the temperature of the material until the decomposition temperature is reached (stage 2). In this stage, combustible gases, noncombustible gases, liquids, carbonaceous residue, and smoke are produced. The combustible gases in turn are oxidized, regenerating additional heat. Carbonaceous residues (or char) are desirable because they preserve structural integrity, retard the outward flow of combustible gases, prevent mixing of air with these gases, and insulate the material from heat that might cause further degradation. This attribute of char is the basis for the fire retardant character of intumescent coatings and some insulating foams.

Dynamics of Burning Materials

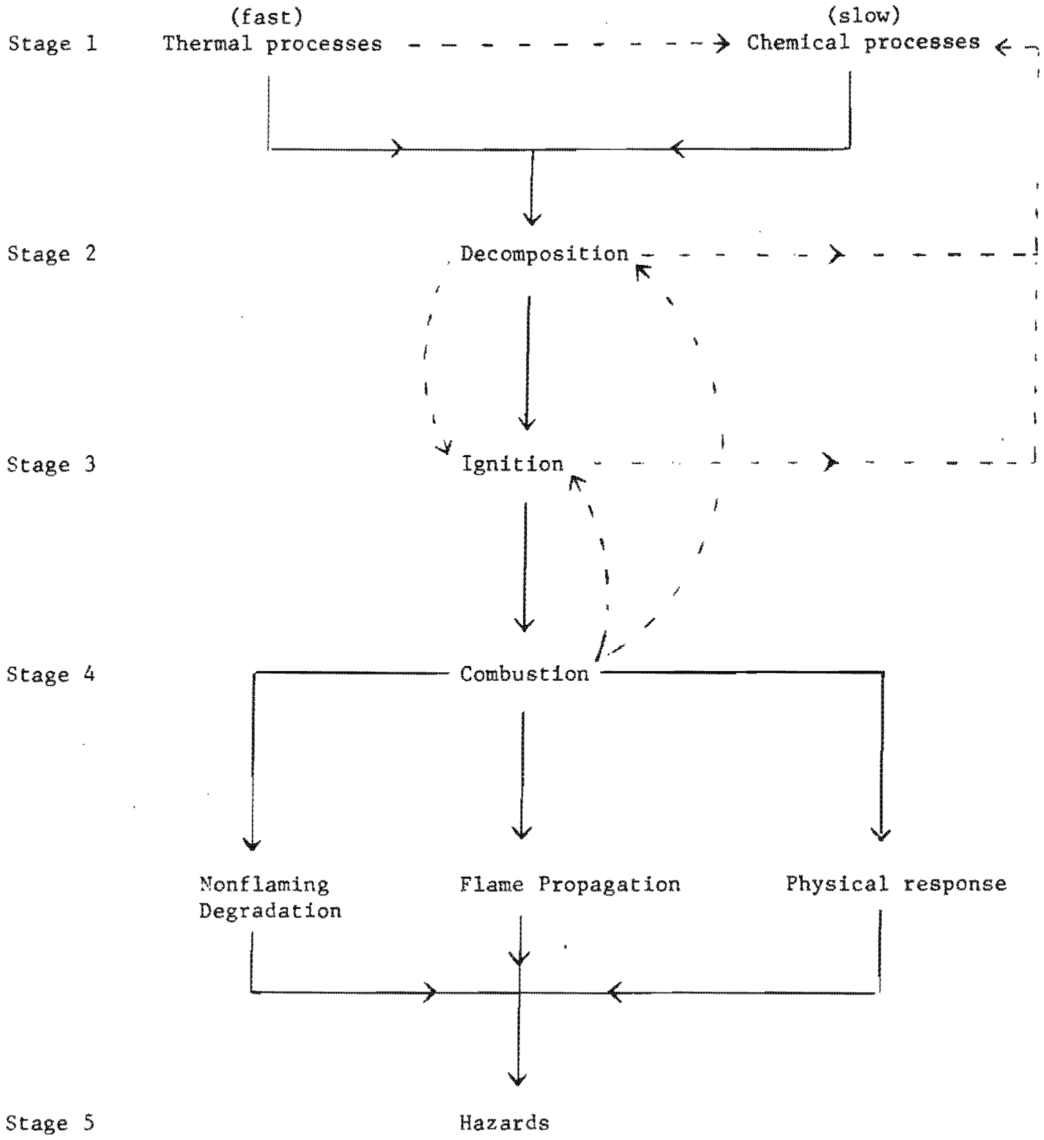

Figure 4.

Stage 3 involves ignition of combustible gases in the presence of sufficient oxidizing agents, in maintaining a self-sustaining reaction within the material.Stage 4 is based on the potential energy within the material, which includes cohesive energy, hydrogen bonding, heat of combustion, and bond dissociation energy. If the net thermal effect of combustion is negative, an external supply of heat is necessary to support burning. In such a case removal of the heat source may result in self-extinction of the fire. If the net thermal effect is positive, the heat excess feeds the fire by increasing the temperature of adjacent material which in turn decomposes and passes from Stage 2 to 3 and so on.

The stage of combustion includes three possible paths: (1) nonflaming degradation, (2) flame propagation, and (3) physical response (shielding, charring, melting). Flame propagation occurs when the net heat of combustion is sufficient to bring the adjacent mass to the burning stage. This depends on the structure and design of the material.

Stages 1 through 4 lead to Stage 5, which is the hazards of the fire, such as heat, smoke, toxic gases, and so on. As previously stated, it is these hazards that fire test methods are designed to evaluate.

Fire Propagation Studies

Scientists at the Spanish Aerospace Institute, Madrid, have made significant contributions to the theory of surface flame propagation (or spread) (28). Their work has led to correlations between theoretical and experimental results, and is similar to American views as espoused by Magee and McAlevy (29, 30) of the Stevens Institute of Technology. According to both research groups, the principal exothermic reaction occurs in the gas phase between volatile combustibles diffusing away from the surface and oxygen going toward it. At a surface location in advance of the flame front, heat from the front causes pyrolysis. The vapors that evolve diffuse away from the surface and are oxidized liberating heat that is fed back to the surface. Taken together, the heat from the advancing flames and the heat fed back from the reaction zone accelerate the vaporization of combustibles and their gas-phase oxidation. This occurrence raises the temperature to the ignition point as the glame front reaches the surface location.

This theory, however, excludes any events that occur in the solid phase. In some cases pyrolysis of the solid phase is significant. Japanese workers (31, 32) have studied the reactions in the condensed phase and have supported the claim that pyrolysis involves the formation of two zones: a pyrolysis zone, which moves into the solid away from the surface as the material is vaporized, and a char zone between the surface and the pyrolysis zone. Primary degradation occurs in the pyrolysis zone. Secondary burning will occur in the char zone if oxygen can enter it and participate in exothermic reactions with combustible vapors or char surfaces.

Recent studies into flame spread phenomena include the work of Mizutani (33) at Osaka University. Here attempts were made to examine the mutual effects between a flame and the aerodynamics (or turbulence). The existence of turbulence increases the flame velocity, while the flame augments the intensity of turbulence. A series of equations for calculating turbulent flame velocities over a wide range of conditions was proposed. These relationships are claimed to help clarify the interactions of flame and aerodynamics, and thereby provide some explanation of flame structure and propagation.

The study of turbulent flames also has been investigated at the Lotnictwa Institute, Warsaw (34). The workers applied chemiluminescent measurements in the study of the structure of turbulent flame. Although the use of chemiluminescence is not new in this endeavor, the workers propose that their techniques have removed the deficiencies of previous experiments. Their technique involves using a microphotometer that can measure local radiation inside the combustion region. Since the intensity of the local radiation is assumed to be proportional to the mass rate of chemical reaction at that point, measurement of this radiation may reveal the fine structure of flames. The effects of aerodynamics on turbulent flames also have been studied by Russian workers (35).

MATERIALS

General

The rapid expansion of polymeric materials in civilian and/military end-items coupled with the concern over their potential combustion hazards have led to the continuing search for improved fire suppressant materials. Civilian applications include clothing, automobile and airplane interiors, intumescent paints, building materials, and home furnishings. Military uses include protective clothing, aircraft and ship insulating materials, electrical components, structural composite reinforcements and matrices, high performance adhesives, ablatives for aerospace systems, and a host of other uses.

Fire resistant polymeric materials can be divided into two categories: those that have inherent fire resistance (e.g. polybenzimidazoles, polyimides, polytetrafluoroethylene, etc.) and those that required modification to become fire resistant (e.g. as in most conventional polymers, such as cellulosics, polyethylene, polystyrene, etc.).

Inherently fire resistant polymers possess certain basic chemical structural features that may include (1) the presence of halogen, phosphorus, or metallic atoms throughout the polymer chain, (2) extensive conjugation along the chain due to aromatic and heteroatomic moities in the polymer backbone, (3) stereoregularity of side chain moities, (4) strong intermolecular attractions, and (5) high cross-link density. The use of inherently fire resistant materials is generally restricted to special applications since their production costs are sometimes prohibitive. This is especially true for high temperature and high performance materials, such as polyimides, polybenzimidazoles, fluoroelastomers, and aromatic polyamides. These organics are used extensively in military and space systems.

Large civilian markets usually rely on the less expensive method of imparting fire resistance to conventional polymers by the use of retardants.

Fire retardants can be classified into three categories. They are,

1. reactive type- the retardant reacts chemically with the polymer components, and is combined chemically into the basic polymer structure.
2. additive type- the retardent is physically blended into the base polymer prior to conversion tc the final product.
3. coadditive type- includes compounds which alone may not be flame retardants, but in the presence of other additives synergistically provides fire resistant properties.

Examples of reactive type retardants are (1) chlorendic acid (sometimes called HET acid) for unsaturated polyesters, (2) phosphorus-containing polyols for polyurethanes, (3) halogenated alcohols for polyurethanes, and (4) brominated bisphenols for polycarbonates, epoxies, and acrylonitrile-butadiene-styrene terpolymers. Polymers that contain reactive type flame retardants have permanent aspects of flame resistance as do materials made of inherently fire resistant polymers. In addition, they are more expensive to produce than materials containing additive or coadditive retardants.

Additive type retardants include (1) phosphate esters for polystyrene, polyurethane foams, and cellulosics, (2) chlorinated paraffins for polyolefins and polyesters, (3) halogenated aromatics for polyolefins, and (4) ammonium halides, ammonium phosphates, metal-amine complexes, and antimony trioxide for polyurethanes.

Coadditive retardants include (1) nitrogen-containing compounds, such as urea and melamine in conjunction with phosphates for cellulosics, (2) phosphates in conjunction with halogenated compounds for cellulosics, and (3) antimony trioxide used with chlorinated substances for phenolics and as fire protective coatings.

The great drawback in the use of flame retardants is that materials containing them generally produce increased amounts of smoke upon combustion. In some cases proper selection of flame retardants and other ingredients can reduce smoke evolution and still retain low flammability. The technically sophisticated nations recognize the problem; however, present technology is insufficient to resolve the situation.

Some of the significant contributions made by foreign nations in the development of fire resistant materials are presented.

United Kingdom

The United Kingdom has developed many fire resistant materials. Courtaulds Limited produces a modacrylic fiber called TEKLAN (36). It is intended for use in protective clothing and is made of vinylidene chloride-acrylonitrile (50:50) fibers. TEKLAN is similar to "Verel" fiber made by Eastman Kodak. Courtaulds also has developed a textile material they call "Heat Shield" which is made of TEKLAN and glass fibers. This blend has the added strength and dimensional stability required for protective clothing in arduous applications such as fire rescue work.

A new polyimide adhesive has been developed at the Royal Aircraft Establishment in Fairnborough (fig. 5) (37). The polyimide contains fluorocarbon linkages in the polymer backbone. These bridging groups provide built-in flexibility to the polymer chains, lowering the glass transition temperature and providing greater "wettability" to the surfaces being bonded. This fire resistant polyimide adhesive is intended mainly for metal-to-metal bonding in high performance aircraft.

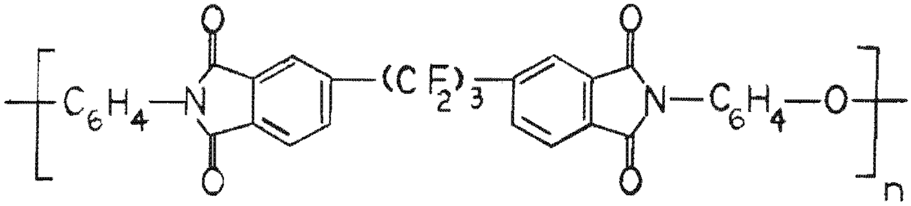

Figure 5

A cold cure phenolic prepeg was developed by the British Aircraft Corporation (BAC) for use in the interior of the Concorde (38). The laminate has low smoke emission properties and is faced with polyvinylfluoride film to provide improved fire behavior. Another fire resistant material used in the Concorde is glass filled nylon 6-6 employed as fittings. The nylon matrix is called MARANYL, made by Imperial Chemical Industries (ICI). These materials are significant in that they are being used where smoke and toxicity requirements are important.

The UK also is a manufacturer of intumescent coatings. Scott Bader Limited manufactures a polyester intumescent resin called CRYSTIC FIREGUARD 75 PA (39). It is intended for use as protection for laminates, fiber board, and wood. It is rated as Class 2 by BS 476: Part 7 and Class 0 by BS 476: Part 6. Scott Bader also supplies fire resistant paint, POLIDENE, made of poly(vinylidene chloride) containing calcium carbonate as the blowing agent (40).

The International Wool Secretariat (London) recently (July 1973) reported the development and testing of a fire resistant wool blend (41). The wool was treated with potassium titanium hexafluoride and potassium zirconium hexafluoride during the dyeing stage.

The British also produce fire retardant grades of polyacetal (polyoxymethylene) called KEMATAL made by ICI, and polypropylene called PROPATHENE also made by ICI (42).

A significant development in the UK is the growing use of polyisocyanurate foams in lieu of the more flammable polyurethanes (8,43). Polyisocyanurates are inherently fire retardant and usually require no further additives. They also produce less smoke upon combustion than do polyurethane foams. Isocyanurate foams initially were developed by NASA as potential insultating materials for aerospace vehicles (19). Their decomposition temperature is 300° C, while that of polyurethanes is less than 200° C. Consequently, isocyanurates have an improved char yield, which helps to retard the penetration of a fire into the material and reduces surface flame spread.

The main monomer used in isocyanurate production is 4,4$'$-diisocyanatodiphenyl methane. The polymer structure is characterized by the isocyanurate ring system, resulting from the cyclic trimerization of isocyanate moieties (fig 6). Materials containing these groups are inherently cross-linked and thereby possess high rigidity and brittleness. Special processing is required to reduce the brittle character. The ICI company manufactures an isocyanurate foam called HEXAFOAM (8). They recommend its use as insulation in buildings where the fire hazards of polyurethane foams cannot be tolerated. HEXAFOAM was rated as Class 1 in the surface spread of flame test (BS 476: Part 7), and was approved by the British Board of Trade for use on ships as insulating panels. This is significant since fire and smoke evolution in confined sections of ships is regarded as a serious hazard.

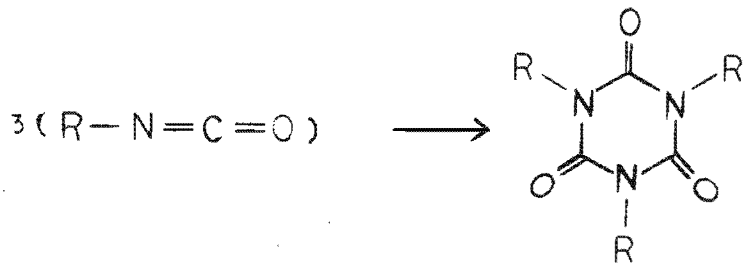

Figure 6.

The British company Plaschem Limited also manufactures an isocyanurate foam called SFR Board (43). When this insulation is faced with asbestos sheeting, it can be used in building construction. According to Plaschem an accidental fire in a London building, which was still under construction showed that even uncoated SFR Board provides excellent fire suppressant and smoke evolution properties. Ceilings made of this uncoated material were exposed to the full brunt of the flames. After the fire was extinguished, it was found that the SFR Board was heavily charred and had begun to curl away from the beams. However, most of the material was still attached to the ceiling beams, thereby affording considerable protection to the wood.

Other nations also are employing isocyanurates instead of urethane foams. In Japan, the Nisshin Spinning Company has patented a process for polyisocyanurate production (<u>44</u>). Investigation into the manufacture of isocyanurates is underway in Germany and France, who along with the Netherlands have tested this new class of material according to their national fire test methods (<u>45</u>). Polyisocyanurate was rated "difficulty combustible" according to German DIN 4102, Class 1 according to Dutch NEN 1076 (flame spread and flashover tests), and nonflammable and not-ignitable according to the French "Epiradiateur" Test.

France

The Société Rhovyl has pioneered the commercial development of poly(vinyl chloride) fibers (36). These inherently fire resistant materials are manufactured by dry-spinning the unmodified polymer from carbon disulphide solvent mixtures. Both filament and staple fiber are produced with various degrees of heat stability. Trade names include RHOVYL, RETRACTYL, and CLEVYL. RHOVYL 55 shrinks 55 percent when heated to 100° C. This is compared to standard PVC fiber which appreciably shrinks below 70° C. PVC fibers are used in curtains, upholstery, blankets, filter cloths and work clothing. They, however, are not resistant to dry cleaning solvents such as trichloroethylene and perchloroethylene. To remedy this, the Société Rhovyl has developed "M" fibers which are produced from syndiotactic poly(vinyl chloride). This class of fibers not only has improved solvent resistance but also has enhanced heat stability. It should be noted that poly(vinyl chloride) fibers are not produced in the United Kingdom or the United States.

Rhone-Poulenc Textiles has developed a poly(amide-imide) fiber called KERMEL (46,47). The basic polymer is based on trimellitic acid anhydride that is polymerized with an aromatic diisocyanate (fig 7).

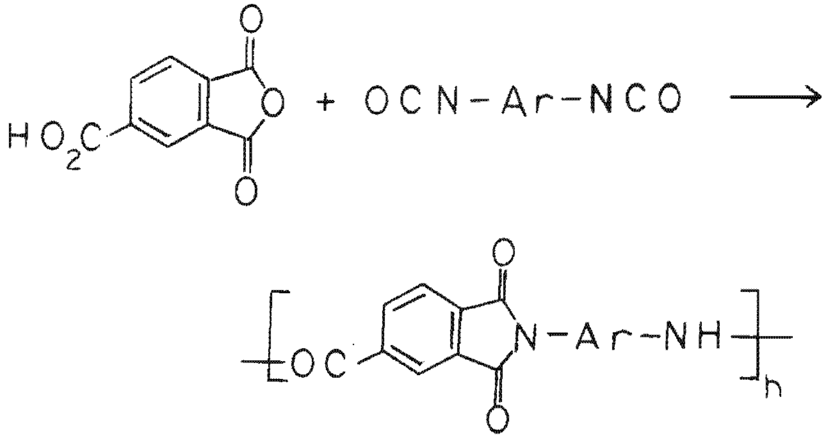

Figure 7.

These polymers have various applications that include electric insulation, adhesives, and fibers. They are characterized by high thermal stability, good dimensional stability, and inherent fire resistance.

At the NATO meeting on Combat Clothing and Equipment, held in February 1973 at Brussels (48), France indicated that they were experimenting with the use of KERMEL in underwear and overalls for armored vehicle crewmen. Their tests involved exposing dummies wearing this underwear and overalls to hydrocarbon fires. France reported that mass production of KERMEL protective clothing was feasible, when considering the permanence of effect, the durability of the fabric, and the cost of production. Poly(amide-imides) are also produced in Japan, West Germany, and the United States.

Rhone-Poulenc has applied for a German patent on a fire resistant carbon filled poly(amide-imide) fiber (49). The material is based on 4,4'-diisocyanatodiphenylmethaneterephthalic acid-trimellitic anhydride copolymer and 8-35% active carbon. It is proposed that the fiber could be used as hot and hazardous gas filters.

Rhone-Poulenc also produces polyimide fibers under trade names KINEL and KERIMID (36). These fibers also are inherently fire resistant and have higher thermal stability compared to KERMEL.

The base polymer has the illustrated structure (fig 8).

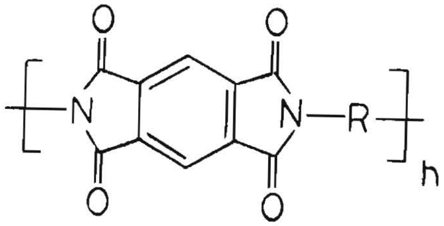

Figure 8.

West Germany

Industry in West Germany appears to produce a large variety of flame resistant plastics made of conventional polymers rendered flame retardant by the use of additives (42,50). Bayer AG produces fire retardant cellulose acetate molding compound (trade name CELLIDOR), nylon-6 resin (trade name DURETHAN), polycarbonate (trade name MAKROLON), and polyurethane foams (DESMOPHEN). Self-extinguishing materials, as tested by ASTM D635-68, include high density polyethylene (VESTOLEN by Chemische Werke Huls AG), high impact polystyrene (HOSTYREN by Farbwerke Hoechst AG), nylon 6 (ULTRAMID by BASF), and polystyrene foam (STYROPOR by BASF). The technology employed in their manufacture appears similar to that used by US industry. This also is true of the German fiber finishing techniques (51).

A noteworthy material developed by Papierfabrik Scheufelen is a fire resistant paper (52) that has been used in the US Apollo program (53). The paper may be similar to one that Scheufelen described in the patent literature (52). It is reported that the paper consists of glass, asbestos, or poly(vinyl chloride) (20-70%), is treated with melamine-formaldehyde resin or PVC, and then is coated with PVC.

The Gustaf Fischer Company, in Haag, is marketing fire resistant flight gloves. They sell for 20 Deutsch Marks per pair, are backed with "Nomex" fabric,and have a leather palm. It is claimed that these gloves currently are in use in the West German Air Force. It should be noted that although "Nomex" was first developed by DuPont in 1960, it is available to many other foreign nations including Japan and the Soviet Union. The base polymer of "Nomex" is poly(m-phenylene isophthalamide) and is inherently fire resistant. It is used in the US Army as protective clothing for helicopter crewmen.

Japan

The Japanese produce a large variety of fire retardant materials. They rely heavily on the use of additive and coadditive retardants for fibers, and they have expressed the continued use and production of such systems since costs are not prohibitive for growing clothing markets (54).

Nonetheless, Japanese scientists have made significant contributions in the area of inherently fire resistant fibers as well.

The Toyo Spinning Company has reported the development of a fire resistant polyester fiber, modified with a phosphorous compound before spinning (54). At this point, it is not known whether the treatment involves reactive or additive retardants. Production was to have begun in the fall of 1972. It is a well known fact that polyester fibers are difficult to render fire resistant, primarily because the processing temperatures for polyester are higher than the decomposition temperatures of conventional additives (55). The fiber developed by Toyo may involve some improved processing techniques which could be a significant contribution to fiber technology.

In 1965, the Kohjin Company developed polychlal fibers whose original trade name was CORDELAN but now is KOHJIN (36). These inherently flame resistant fibers are made of poly(vinyl chloride) and poly(vinyl alcohol) (50:50). Apparently, poly(vinyl alcohol), grafted with PVC, is spun from a solution containing additional PVC. This method enables a high percentage of PVC to be incorporated into the fiber. Polychlal fibers are commercially available, and have high thermal stability (up to 170° C), and chemical and solvent resistance. Practical applications are in carpets, blankets, clothing, and upholstery. The significance of these materials, of course, is their combined low cost and high fire resistance.

The Japanese also manufacture modacrylic fibers, as is done in the UK and the United States (36). The Kanegafuchi Spinning Company produces a vinyl chloride/acrylonitrile (60/40) fiber called KANEKALON. The US analog is "Dynel," produced by Union Carbide. KANEKALON, like the British "Teklan," is suitable for use in fire protective clothing.

In 1972, it was reported (56) that the Kanegafuchi Spinning Company, Mitsubishi Chemical Industries, and the Carborundum Company (USA) were combining efforts to try to commercialize "Kynol" fibers (36). These inherently fire resistant fibers were developed first by Carborundum, and are described as highly cross-linked phenolic polymers. The material is flame resistant to an oxyacetylene-torch, but is not highly heat resistant since charring occurs at about 260° C. Applications include protective clothing and aircraft and aerospace components. The "Kynol" fibers are in the same price range as "Nomex" fibers, which the Teijin Company began to sample market in 1972 (54).

The Nitto Boseki Company has begun marketing an inherently flame resistant fiber called TAYENTEX. It is similar to "Pluton" fiber made by the 3M Company. TAYENTEX is a carbonized fiber, probably made by thermolyzing polyacrylonitrile. It will not burn when exposed to an oxyacetylene flame of 2760° C, but only has moderate thermal stability (decomposing at 300° C). Unlike carbon fibers, TAYENTEX does not conduct electricity. Chemical analysis indicates that it consists only of carbon, hydrogen, nitrogen, and oxygen. Manufacturing details of course are proprietary. Potential applications include filter clothes, electrical insulation, thermal insulating mats and fabrics, and protective clothing. Its current low tenacity (1.0 - 1.5 grams/denier), as well as its cost (55 dollars per square yard), restricts its use in commercial clothing. It is claimed, however, that TAYENTEX matting is used as insulation in the Japanese C-1 aircraft.

A further contribution to fiber technology is the manufacture of a low cost carbon fiber, developed by the Mitsubishi Oil Company. A continuous carbon filament is produced from the asphalt residue that remains after the vacuum distillation of petroleum. This residue is treated chemically giving a "special pitch" from which preliminary fibers are spun. The company currently is marketing samples, although their quality is lower than carbon fibers produced by the pyrolysis of cellulosic and acrylic fibers. Nevertheless, the planned price proposed by Mitsubishi is about 10 dollars a kilogram. This is markedly low compared to the current price of 88 dollars a kilogram for carbon fibers made by other methods.

Japanese industry produces many fire resistant resins, and is continuing to conduct research toward the development of new classes of materials appropriate for commercialization. A few of these commercial grades are listed in Table 5.

Table 5. Some Japanese Fire Resistant Resins

Trade Name	Resin Type	Producer
Tufrex	Acrylonitrile-butadiene-styrene (ABS)	Mitsubishi Oil
Iupilon N-2	Polycarbonate	" "
Diarex	Polypropylene	" "
Idemitsu	Polycarbonate	Idemitsu Petrochemical
Toray	Nylon 66	Toray Ind.
Klintate	Polyolefin	Sumitomo
Styrol	Polystyrene	Denki Kagaku
Sumikon	Phenolic	Sumitomo
Hitachi	Polyester Molding Compound	Hitachi Chemical
Nipeon-Graftmer	PVC	Japanese Geon
Paifron	Poly(amide-imide)	Hitachi

Other companies that manufacture fire resistant polymeric materials include Asahi Chemical, Matsushita Electric, Shin-Etsu Chemical, Furukawa Electric, and Teijin Limited.

A new aromatic polyester, called UP POLYMER, is advertised as an inherently fire resistant thermoplastic (self-extinguishing by ASTM D-635-68) (57). The material is manufactured by Unitika Limited, and is based on the copolymer of isophthalic acid and a bisphenol. Thermal deformation temperature is 164° C at a load of 18.6 kg/cm^2. In addition, the material is reported to have high impact resistance and high transparency. The thermoplastic can be molded and formed easily, and has potential application in electrical components, films, and packaging. According to Unitika, the material will be commercially available in 1974 at a proposed price of about 30 dollars a kilogram.

The Unitika Company has asked for patent rights on a new fire resistant foam based on a mixture of poly(vinyl alcohol), poly(vinylidene chloride), and vinylidene chloride-vinylchloride copolymer (58). Little more is known about the foam, but it does incorporate some of the fire retarding features of the modacrylic and polychlal fibers mentioned earlier.

Japanese researchers at Yamagata University have prepared a new class of high temperature polymers, poly(amide-benzothiadiazine dioxides), by the two-step cyclopolymerization of diaminobenzensulphonamides and aromatic bisacyl chlorides (fig 9) (59).

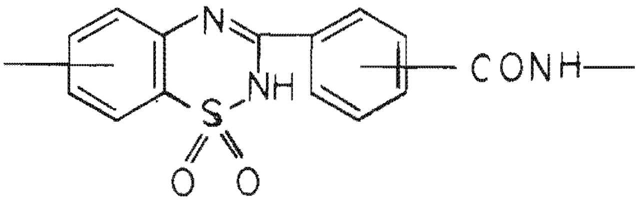

Figure 9.

The polymer has a decomposition temperature of 450-470° C, and exhibits self-extinguishing properties upon exposure to a free flame. No doubt this type of effort is predominantly oriented toward basic research, yet it represents the considerable attention the Japanese are giving to the problem of flame resistant materials.

USSR

The Soviet Union does not appear to be emphasizing the development of fire resistant organic materials based on conventional polymers as much as other technically advanced nations have. Nonetheless, Soviet researchers (60-66) have investigated the use of halogen-containing and phosphorous-containing reactive additives for flame retardant polyester resins, polycarbonates, cellulosic fibers, and acrylics. Much of the work concerning textiles has been done at the Moscow Textile Institute under Z. A. Rogovin (61-62), at the Leningrad Institute of Textile and Light Industry under A. I. Meos and L. A. Vol'f (63), and at the Scientific Research Institute of Chemistry and Technology of Cotton Cellulose under A. Yuldashev (64).

On the other hand, the Soviet Union has an extensive research program in high temperature polymers. Some of these materials are appropriate for use as inherently fire resistant adhesives, fibers, coatings, and plastics in aerospace and high performance aircraft systems (67). Into this category fall Soviet polyimides, polyarylates, polybenzimidazoles, polytetrafluoroethylene, aromatic polyamides, and others. The main Soviet researchers in this field include V. V. Korshak (68), A. A. Berlin, and M. M. Koton.

The Soviets claim to have production capabilities in many of these fire retardant polymers, patterning much of the necessary technology after that in the United States and other Western countries. Some of these materials are summarized in Table 6.

Table 6. Soviet Fire Resistant Polymeric Materials

Trade Name	Polymer Type
Phenylon	poly(m-phenylene isophthalamide)
Khlorin	chlorinated PVC fiber
Sulfon-T	aromatic sulfonated polyamide
Arimid	polyimide
Oksalon	polyoxadiazole
Arilon	polyarylate
PIOD	polyimidoxadiazole
Floroplast	polytetrafluoroethylene resin
Polifen	polytetrafluoroethylene fiber
Ftorlon-3	poly(monochlorotrifluoroethylene)
Kartilon	polybenzoxazole

The Soviets also claim to have developed a high-modulus, high temperature, and fire resistant fiber they call VNIIVLON-N (69). The material was reported in 1971, and judging from the claimed physical properties, it may be akin to "Fiber B" or "PRD-49," both made by DuPont. Other fire retardant materials available to the Soviet Union include polyphenylenesulphides, polysulphones, and metal-containing and silicon-containing polymers.

Soviet polyimides are used in PAK-1 lacquer, PM films, DFO molding materials, SP-1 adhesives, and as binders in STP-1 glass-reinforced plastic. Polyarylates are used in AMAN self-lubricating materials which were employed as bearings for the Lunokhod moon rover vehicle. Soviet polybenzimidazoles also appear to find extensive military applications.

In addition to those materials already mentioned, the Soviets use polysiloxanes and fluoroelastomers as high temperature and fire resistant elastomers, and they are conducting research in polyphosphazene (70) and carboranesiloxane (71) elastomers.

Conclusions

This brief overview of the fire hazard problems of organic polymers certainly does not attempt to resolve the difficulties. It can only hope to bring the problem and the world-wide efforts to solve the problem into better focus. As one analyzes the foreign efforts, one observes that they appear to coincide both in scope and intensity with those of the United States.

The stated deficiencies of current fire, smoke, and toxic vapor testing methods have been realized by all concerned. It appears that the remedy essentially must involve a research approach to develop scientifically sound and reliable tests that can predict the behavior of a material in an actual fire. In this vein, the standardization of reliable tests must follow, and perhaps this standardization might be most effective if it eventually attains international recognition. This of course necessitates world-wide cooperation, which at this time is only just beginning.

A complete understanding of the dynamics of fire also must include a research approach, and lead to the ability to predict the fire hazard problems posed by organic materials. This contribution would effectually lead to an improvement of material design and composition. Revisions of material consistency and design certainly have to be based on research, technological, and economic considerations. The current reliance on conventional polymers rendered fire resistant by the use of additives probably will continue primarily because of their relative cheapness. The added smoke and toxic vapor hazards posed by them, however, must be relieved.

A subjective aspect of fire safety that has thus far not been mentioned is the need for unambiguous legislation and mandatory enforcement of regulations or codes that govern the use of all types of organic materials in civilian as well as military items. This aspect is obvious, but nonetheless may be the most difficult to obtain.

REFERENCES

1. Emmons, H.W., Fire Res. Abstr. Rev., 10, 133 (1968).
2. Chemical and Engineering News, p.9, July 16, 1973.
3. Hanlon, J. and L. McGinty, New Scientist, p.306, August 9, 1973.
4. Scott, K.A., Brit. Polymer J., 2, 244 (1970).
5. Malhorta, H.L., "Significance of Fire Tests for Plastics," Plastics and Polymers, 41 (151), 44-49 (1973).
6. Kelley, R.T. and W.W. Stevenson, "The Use of Plastics in Building, With Particular Reference to Their Performance in Fires," Plastics and Polymers, 41 (151), 28-34 (1973).
7. Wicker, G.L., PRT Polymer Age, pp.298-300, August, 1972.
8. Wilson, W.J. et al., Plastics and Polymers, 40 (149), 290-303 (1972).
9. Stamm, G. "The Present State of Flammability Testing of Textiles," Textilveredlung, 6 (10), 656-660 (1971).
10. Breden, L.H., "World Index of Plastics Standards," National Bureau of Standards Special Publication 352, 1971, 458 pages.
11. Feikema, J.G., TNO-Nieuws, 27 (7), 361-370 (1972).
12. Sakui, S., Technocrat, 6 (7), 58 (1973).
13. Pal, K., "Flame Retarder Efficiency Test," Muanyag Gumi, 9 (6), 177-178 (1972).
14. Fainshtein, B.M. and K.Z. Fattakhov, Plast. Massy, (6) 66-67 (1969).
15. Furuya, M. Sen'i Gakkaishi, 29 (3), 8-11 (1973); Chem. Abstr., 78, 137237n (1973).
16. Wogrolly, E. G. and K. A. Scott, Osterr. Kunststoff-Zeitschrift, 4 (3-4), 51-56 (1973).
17. Imhof, L. G. and K.C. Steuben, Polymer Eng. Sci., 13 (2), 146-152 (1973).
18. Reinke, R. E. and C. F. Reinhardt, Modern Plastics, pp. 94-98, February 1973.
19. Riccitiello, S. R. and K. W. Heising, "The Application of Space Program Fire-Resistant Technology to Housing," NASA TN D-7370, August 1973.

20. Waterman, T. E., IIT Research Institute Project M6131 for Defense Atomic Support Agency, DASA Report 1886, September 1966.

21. Rumberg, E. "Disintegration Products and Smoke Generation During Fire Action on Plastics," Ver. Deut. Ing., 113 (4), 277-280 (1971).

22. PRT Polymer Age, p.140, April 1973.

23. PRT Polymer Age, p.141, April 1973.

24. Aviation Week and Space Technology, p.28, September 10, 1973.

25. Einhorn, I. N., J. Macromol. Sci. Revs. Polymer Technol., D1 (2), 113-184 (1971).

26. Effenberger, E., "Toxic Effects of the Combustion Products of Plastics," Stadtehygiene, No. 12, 275-280 (1972).

27. Kishitani, K., J. Fac. Engr., Univ. of Tokyo, (B) 21, 1 (1971).

28. Sanchez Tarifa, C. et al., 12th Int. Symp. Combust., 229-240, The Combustion Institute, 1969.

29. Magee, R. S. and R. F. McAlevy, J. Fire Flammability, 2, 271-297 (1971).

30. Hilado, C. J., Chem. Tech., 2 (4), 232-237 (1972).

31. Matsumoto, T. et al., 12th Int. Symp. Combust., 515-524, The Combustion Institute, 1969.

32. Kinbara, T. et al., 11th Int. Symp. Combust., 525-531, The Combustion Institute, 1967.

33. Mizutani, Y., "Amplification of Turbulence Level by a Flame and Turbulent Flame Velocity," Combustion and Flame, 19, 203-212 (1972).

34. Chomiak, J., "Application of Chemiluminescence Measurement to the Study of Turbulent Flame Structure," ibid., 18, 429-433 (1972).

35. Vulis, L. A. et al., Gorenie Vzryu, Mater. Vses. Simp. 3rd 1971, 330-336; Chem. Abstr., 78, 161705j (1973).

36. Collins, J. R., Plastics and Polymers, 40 (149) 283-289 (1972).

37. Chemical and Engineering News, p.16, July 30, 1973.

38. PRT Polymer Age, "Polymers in Aerospace," pp.374-375, October 1972.

39. PRT Polymer Age, p.33, January 1972.

40. Allsebrook, W. E., Paint Manufacture, pp.40-44, November 1972.

41. Chemical and Engineering News, p.9, July 23, 1973.

42. "Modern Plastics Encyclopedia" McGraw-Hill, 1972.

43. PRT Polymer Age, "Case History: Polyurethane Foam in Fire," p.178, May 1973.

44. Ashida, K., "Heat and Flame Resistant Polyisocyanurate Foams," Japan 71 42,386; Chem. Abstr., 76, 142000t (1972).

45. Diehr, H. J. et al., Kunststoff, 62, 731-732 (1972).

46. Chambion, J., Chimie et Industrie, 106 (7) 453-458 (1973).

47. Pigeon, R., Textilia, 17 (7) 35-39 (1971).

48. Report of Meeting (NATO) on Combat Clothing and Equipment, February 1973.

49. Buisson, F., Ger. Offen. 2,239,707; Chem. Abstr., 78, 148872s (1973).

50. Jenker, H., Kunststoff, 62, 690-692 (1972).

51. Einsele, U., Textil-Praxis Int., 27 (3), 172-175 (1972); 27 (4), 224-227 (1972).

52. Brintzinger, H., Ger. Offen. 1,817,535; Chem. Abstr., 75, 7672c (1971).

53. Conference on Materials For Improved Fire Safety, NASA SP-5096, 1970.

54. Technocrat, 5 (8), 38 (1972).

55. Baum, B. M., Chem. Tech., pp.416-421, July 1973.

56. Technocrat, 5 (5), 38 (1972).

57. ibid., 6, (5), 34 (1973).

58. Sumi, M., Japan. Kokai, 73 19,653; Chem. Abstr., 79, 32505r (1973).

59. Imai, Y. and H. Koga, J. Polymer Sci., 11, 289-300 (1973).

60. Li, P. Z. et al., Plast. Massy, (5)15-19 (1963).

61. Rogovin, E. E., Zhur. Priklad. Khim., 40 (1), 177 (1967).

62. Rogovin, E. E., ibid., 40 (2), 413-417 (1967).

63. Vol'f, L. A. et al., Otkrytiya, Izobret. Prom. Obraztsy, Tovarnye Znaki, 47 (3), 73 (1970); Chem. Abstr., 72, 134023e (1970).

64. Yuldashev, A., Dokl. Akad. Nauk. Uzb. SSR, 25 (9), 30-31 (1968).

65. Kolesnikov, G. S. et al., ibid., 46 (35), 74 (1969).

66. Razinskaya, I. N. et al., Plast. Massy, (3), 11-12 (1973).

67. Abduragimov, I. M. et al., "Aspects of the Development of Fire Resistant Materials for Aerospace Applications," Kosmicheskie Issledovaniya, 9 (6), 934-939 (1971).

68. Korshak, V. V., "The Chemical Structure and Thermal Characteristics of Polymers," Jerusalem, 1971, 460 pages.

69. Khim. Volokna, (1), 76 (1971).

70. Zhivukhin, S. M. et al., "A Method For Obtaining Phosphonitrilic Polymers," USSR 218,438, Otkrytiya, Izob. Prom. Obraztsy Tovarnye Znaki, 17, 81 (1968).

71. Klebanskiy, A. L. et al., ibid., 48 (9), 86 (1971).