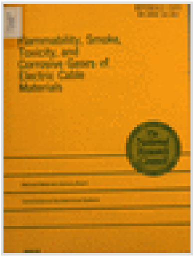


Flammability, Smoke, Toxicity, and Corrosive Gases of Electric Cable Materials (1978)

Pages
168

Size
8.5 x 10

ISBN
0309335450

Task Force on Flammability, Smoke, Toxicity, and Corrosive Gases of Electric Cable Materials; National Materials Advisory Board; Commission on Sociotechnical Systems; National Research Council

NATIONAL RESEARCH COUNCIL
COMMISSION ON SOCIOTECHNICAL SYSTEMS

NATIONAL MATERIALS ADVISORY BOARD

Chairman

Mr. Julius J. Harwood
Director, Materials Science Laboratory
Engineering and Research Staff
Ford Motor Company
P.O. Box 2053
Dearborn, Michigan 48121

Past Chairman

Dr. Seymour L. Blum
Vice President
Northern Energy Corporation
70 Memorial Drive
Cambridge, Massachusetts 02142

Members

George S. Ansell
Dean, School of Engineering
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. Alan G. Chynoweth
Executive Director, Electronic Device, Process and Materials Division
Bell Laboratories
Murray Hill, New Jersey 07974

Dr. Arthur C. Damask
Professor, Physics Department
Queens College of New York City
Flushing, New York 11367
(Mail Address)
29 Brewster Lane
Bellport, N.Y. 11713

Mr. Selwyn Enzer
Associate Director
Center for Futures Research
University of Southern California
Los Angeles, California 90007

Joseph N. Epel
Director, Plastics Research and Development Center
Budd Corporation
356 Executive Drive
Troy, Michigan 48084

Dr. Herbert I. Fusfeld
Director, Center for Science and Technology Policy
Graduate School of Public Administration
New York University
4 Washington Square North
New York, New York 10003

Dr. Robert E. Hughes
Professor of Chemistry
Executive Director, Materials Space Center
Department of Chemistry
Cornell University
Ithaca, New York 14850

Dr. James R. Johnson
Executive Scientist and Director
Advanced Research Programs Laboratory
3M Company
P.O. Box 33221
St. Paul, Minnesota 55133

Mr. Lawrence Levy
President
Northern Energy Corporation
70 Memorial Drive
Cambridge, Massachusetts 02142

Mr. William D. Manly
Senior Vice President
Cabot Corporation
125 High Street
Boston, Massachusetts 02110

Dr. Frederick T. Moore
Advisor, Industrial Development and Finance Department, Room D422
World Bank
1818 H Street, N.W.
Washington, D.C. 20431

Dr. Harold W. Paxton (1978)
Vice President-Research
U.S. Steel Corporation
600 Grant Street
Pittsburgh, Pennsylvania 15219

Dr. Nathan E. Promisel
Consultant
12519 Davan Drive
Silver Spring, Maryland 20904

Dr. Jason M. Salsbury
Director
Chemical Research Division
American Cyanamid Company
Berdan Avenue
Wayne, New Jersey 07470

Dr. Raymond L. Smith
President
Michigan Technological University
1400 College Avenue
Houghton, Michigan 49931

William M. Spurgeon
Director, Manufacturing and Quality Control
Bendix Corporation
24799 Edgemont Road
Southfield, Michigan 48034

Dr. Morris A. Steinberg
Director, Technology Applications
Lockheed Aircraft Corporation
Burbank, California 91520

Dr. Giuliana C. Tesoro
Adjunct Professor
Massachusetts Institute of Technology
278 Clinton Avenue
Dobbs Ferry, New York 10522

Dr. John E. Tilton
Associate Professor
Department of Mineral Economics
221 Walker Building
The Pennsylvania State University
University Park, Pennsylvania 16802

Dr. John B. Wachtman, Jr.
Division Chief
Inorganic Materials Division
National Bureau of Standards
Room B306, Materials Building
Washington, D.C. 20234

NMAB Staff:

W. R. Prindle, Executive Director
J. V. Hearn, Executive Secretary

11/2/78

BIBLIOGRAPHIC DATA SHEET

1. Report No. NMAB-342

2.

3. Recipient's Accession No.

4. Title and Subtitle
Flammability, Smoke, Toxicity, and Corrosive Gases of Electric Cable Materials

5. Report Date
1978

6.

7. Author(s) Task Force on Flammability, Smoke, Toxicity, and Corrosive Gases of Electric Cable Materials

8. Performing Organization Rept. No. NMAB-342

9. Performing Organization Name and Address
National Materials Advisory Board
National Academy of Sciences
2101 Constitution Ave., N.W.
Washington, D. C. 20418

10. Project/Task/Work Unit No.

11. Contract/Grant No.
MDA-903-74-C-0167

12. Sponsoring Organization Name and Address
Department of Defense
National Aeronautics and Space Administration

13. Type of Report & Period Covered

14.
Final

15. Supplementary Notes

16. Abstracts

Organic polymers used as insulation and jacketing materials in electric cables, once ignited, burn and spread fire rapidly. Furthermore these polymeric components generate dense smoke as well as toxic and/or corrosive combustion products that severely limit the ability to control and extinguish a fire.

This report contains the formal papers given at a workshop on flammability, smoke, toxicity, and corrosive gases of electric cable materials and in addition includes summaries of the workshop discussion sessions. Based on these activities, a number of conclusions and recommendations are presented for materials and design; testing for flammability, smoke, and toxicity and, to a lesser extent, corrosive gases; and detection devices.

17. Key Words and Document Analysis. 17a. Descriptors

Flammability
Toxicological Testing
Detection Devices

Wire and Cable Insulations
- PVC
- Fluoropolymers
- Polyimides
- Silicones
- Polyphosphazenes

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group

18. Availability Statement
This report has been approved for public release and sale; its distribution is unlimited

19. Security Class (This Report)
UNCLASSIFIED

20. Security Class (This Page)
UNCLASSIFIED

21. No. of Pages
157

22. Price

THIS FORM MAY BE REPRODUCED

705807 AD-A065 047/3

Flammability, Smoke, Toxicity, and Corrosive Gases of Electric Cable Materials

(Final rept)

National Materials Advisory Board (NAS-NAE), Washington, DC.
Corp. Source Codes: 405114
Report No.: NMAB-342
1978 162p
Errata sheet inserted.
Languages: English
NTIS Prices: PC A08/MF A01
Journal Announcement: GRAI7914
Contract No.: MDA903-74-C-0167

Organic polymers used as insulation and jacketing materials in electric cables, once ignited, burn and spread fire rapidly. Furthermore these polymeric components generate dense smoke as well as toxic and/or corrosive combustion products thet severely limit the ability to control and extinguish a fire. This report contains the formal papers given at a workshop on flammability, smoke, toxicity, and corrosive gases of electric cable materials and in addition includes summaries of the workshop discussion sessions. Based on these activities, a number of conclusions and recommendations are presented for materials and design; testing for flammability, smoke, and toxicity and, to a lesser extent, corrosive gases; and detection devices. (Author)

Descriptors: *Electric cables; *Polymers; Flammability; Smoke; Toxicity; Corrosive gases; Insulation; Organic materials; Jackets; Ignition; Flame propagation; Combustion products; Conferencing(Communications)

Identifiers: NTISDODXA

Section Headings: 9A (Electronics and Electrical Engineering--Components); 11I (Materials--Plastics); 21B (Propulsion and Fuels--Combustion and Ignition); 49F (Electrotechnology--Power and Signal Transmission Devices); 71O (Materials Sciences--Plastics); 81A (Combustion, Engines, and Propellants--Combustion and Ignition)

Flammability, Smoke, Toxicity, and Corrosive Gases of Electric Cable Materials

Report of the
Task Force on
Flammability, Smoke, Toxicity,
and Corrosive Gases
of
Electric Cable Materials

NATIONAL MATERIALS ADVISORY BOARD

Commission on Sociotechnical Systems

National Research Council

Publication NMAB-342
National Academy of Sciences
Washington, D. C.
1978

NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

This study by the National Materials Advisory Board was conducted under Contract No. MDA-903-74-C-0167 with the Department of Defense and the National Aeronautics and Space Administration.

This report is for sale by the National Technical Information Service, Springfield, Virginia 22151.

Printed in the United States of America.

ABSTRACT

Organic polymers used as insulation and jacketing materials in electric cables, once ignited, burn and spread fire rapidly. Furthermore, these polymeric components generate dense smoke as well as toxic and/or corrosive combustion products that severely limit the ability to control and extinguish a fire.

This report contains the formal papers given at a workshop on flammability, smoke, toxicity, and corrosive gases of electric cable materials and in addition includes summaries of the workshop discussion sessions. Based on these activities, a number of conclusions and recommendations are presented for materials and design; testing for flammability, smoke, and toxicity and, to a lesser extent, corrosive gases; and detection devices.

PREFACE

The National Materials Advisory Board of the Commission on Sociotechnical Systems, National Research Council, under a contract with the Department of Defense and the National Aeronautics and Space Administration, was requested to undertake a study on the flammability of and the generation of smoke and toxic and corrosive combustion products by electric cable materials.

A task force consisting of selected members of the Committee on Fire Safety Aspects of Polymeric Materials, technical advisors, and government liaison representatives organized a workshop, which was held at the National Academy of Sciences, Washington, D.C. on May 10-11, 1977.

The proceedings of the workshop, list of participants, and conclusions and recommendations and individual workshop discussions, comprise the material in this report.

TASK FORCE ON FLAMMABILITY, SMOKE, TOXICITY, AND CORROSIVE GASES OF ELECTRIC CABLE MATERIALS

CHAIRMAN

DR. ALFRED GILBERT, Corporate Research and Development, General Electric Company, Schenectady, N.Y.

MEMBERS

DR. FRANK E. KARASZ, Polymer Science and Engineering Department, University of Massachusetts, Amherst, Mass.

DR. ELI M. PEARCE, Chemistry and Chemical Engineering Department, Polytechnic Institute of New York, Brooklyn, N.Y.

TECHNICAL ADVISORS

PROF. ISRAEL KATZ, The Center for Continuing Education, Northeastern University, Boston, Mass.

DR. JACK A. WINSTEAD, Advisory Center on Toxicology, National Academy of Sciences, Washington, D.C.

LIAISON REPRESENTATIVES

Department of the Navy

MR. MICHAEL A. DE LUCIA, David Taylor Naval Ship Research and Development Center, Annapolis, Md.

DR. ERNEST H. HALPERN, David Taylor Naval Ship Research and Development Center, Annapolis, Md.

Department of the Army

DR. GEORGE R. THOMAS, Army Materials and Mechanics Research Center, Watertown, Mass.

Department of Transportation

MR. IRVING LITANT, DoT Transportation Systems Center,
Cambridge, Mass.

Department of Health, Education, and Welfare

MR. RICHARD E. WIBERG, National Institute of
Occupational Safety and Health Morgantown, W. Va.

Department of Energy

MR. Arnold Weintraub, Industrial Safety and Fire
Protection Branch, Washington, D.C.

Department of Commerce

DR. JAMES H. WINGER, National Bureau of Standards,
Washington, D.C.

NMAB Staff

DR. STANLEY M. BARKIN, National Academy of Sciences,
Washington, D.C.

The chairman and members of the task force are Academy-appointed members of the ad hoc Committee on Fire Safety Aspects of Polymeric Materials.

CONTENTS

Presentations

Workshop Summaries

INTRODUCTION

THE PROBLEM

The organic polymers used as insulation and jacketing materials in modern electric cables present a major problem during fire conditions. Although the cables are generally not the source of fire ignition, they are highly vulnerable. Once ignited, they will burn and spread fire rapidly. In addition, their polymeric components--typically, polyethylene, poly(vinyl chloride), polychloroprene, etc.--generate dense smoke as well as toxic and/or corrosive combustion products that severely limit the ability of fire fighters to control and extinguish a fire, threaten the life and health of those exposed, and significantly increase fire damage costs and repair time.

Present cable standards usually encompass only the fire-propagation (flame spread) parameter of a candidate design without regard to its production of smoke or toxic or corrosive products. The traditional approach to increasing the fire retardance of a polymer has been through additives compounded into the material. Although increasing the halogen content of a material will generally decrease its flame spread, it will do so at the expense of increased smoke generation (due to smoldering combustion) and increased toxic and corrosive product generation (increased carbon monoxide and hydrogen chloride gas). A comprehensive evaluation of all fire performance parameters, including flammability, smoke, and toxic and corrosive products, is required to optimize performance.

SERVICE EXPERIENCE

The Navy is especially alert to fire problems along cableways. In recent ships (particularly carriers), cables have been cited as spreading relatively small, confined fires, resulting in substantially increased damage. Voluminous, dense smoke generated by burning cables travels multiple paths along passageways and through hatches, rapidly masking the fire location and hampering both efficient and effective fire-fighting response. Most fire casualties are attributed to smoke inhalation, but severe corrosion of sensitive electrical contacts caused by gases generated during cable fires adds to the repair costs and affects the reliability of equipment, thereby reducing the ship's mission capability. Toxic gas generation during a fire is a major problem in ships (particularly submarines), since evacuation of personnel is generally impossible when the ship is submerged or engaged in combat operations.

RESEARCH AND DEVELOPMENT EFFORTS

The final report of the Presidential Commission on Fire Prevention and Control, "America Burning," focused attention on the scope and gravity of the nation's fire problem. As a consequence, many government agencies, universities, societies, and private corporations have initiated or expanded fire research programs. Most efforts have been product-oriented, empirical, and based on the use of additives to improve one aspect of fire performance. Very little work has been addressed to cables specifically. The Institute of Electrical and Electronics Engineers (IEEE) did publish a new, standard, vertical-tray cable flammability test to improve the evaluation of flame spread of nuclear power plant cables but did not address the consequences of the smoke and toxic and corrosive products of combustion. Each application is unique, and a systems approach toward a solution is required. For example, a highly toxic, fire-retardant additive may be acceptable for a generating station cable application but entirely unacceptable in a nursing home or submarine environment.

MEANINGFUL TESTS FOR FLAMMABILITY, SMOKE, TOXIC PRODUCTS, AND CORROSIVE GASES

With the foregoing in mind, it becomes evident that there is a need for meaningful flame-spread tests to help evaluate the ability of cable bundles and systems to spread fire. These tests should reflect the materials and geometry of the cable systems and indicate the probable flame spread in a shipboard environment. Moreover, a cable, smoke test is needed for the evaluation of smoke generation from cable materials. Heavy smoke not only prevents personnel from evacuating an area by obscuring exit signs or the location of fire but also does not permit personnel in damage control parties to fight the fire and perform other damage control tasks. Toxic-gas evolution tests are required to gain an understanding of means for protecting personnel for evacuation and damage-control purposes. Corrosion tests are needed to ensure the reliability of electrical contacts and connections, thereby guaranteeing appropriate ship performance. Additionally, these four test areas must be optimized to assure survivability and performance of ships as well as performance by personnel of their military functions.

EARLY DETECTION

Sensors and cable systems are needed to detect early pyrolysis products evolved by heating and burning of polymers. Early fire warning can prevent cable destruction and flame spread.

ADVANCED MATERIALS

The need for nonburning dielectric materials for use in cables should be stressed because present-day organic dielectrics spread fire, smoke, toxic products, and corrosive gases. Such materials might be organic-inorganic systems (for example, silicones) that could minimize the fire problems associated with cables.

In a totally inorganic system, problems of flexibility, film thickness, and dielectric properties under humid conditions may make it difficult to fabricate effective cables. Much thought and effort in materials work are required to resolve the problems of producing a flexible, dielectric, inorganic film bonded to a conductor in order to make a cable that will not burn, smoke, or give off toxic products and corrosive gases. The investigation of dielectric properties of inorganic films is also related to the problem of corrosion of metals. Some contributions by people versed in corrosion theory and dielectric films would be useful. Although ceramic coatings and tubing have been used as cable insulation by the Navy for several decades, the need for flexibility, sealability, and frequent maintenance makes it highly advisable to continue the search for other inorganic systems.

CONCLUSIONS AND RECOMMENDATIONS

Based on the presentations and workshop discussions, the task force arrived at the following conclusions and recommendations.

MATERIALS AND DESIGN

Conclusions

1. Poly(vinyl chloride) (PVC) and polyolefins are, and will remain in the near future, the primary insulating materials used in wire and cable insulation. Many factors, but primarily economics, dictate their continued use.

2. PVC is used as a generic name, but flammability and smoke properties vary widely as a function of specific cable formulation.

3. PVC can be an acceptable insulating and jacketing material if care is taken with respect to cable installation, fire-extinguishment systems, prevention measures, and maintenance of all systems. Especially critical may be its use in submarines.

4. Fluoro-olefins will receive increased attention because their unique combination of dielectric, chemical, and thermal properties make them desirable for use as wire insulations. However,because of the higher cost of these materials they are best suited for specialized applications such as aboard a submarine where a fire could lead to more disastrous consequences than on a surface ship. There may be certain problems associated with their use caused by the toxicity of combustion products.

5. Polyphosphazenes are emerging as a new class of higher-priced materials to consider and are beginning to be marketed on a limited basis. With this exception there are no other new, identified, more fire-resistant materials approaching commercialization.

6. In selected applications, overall risk-benefit analysis can dictate the use of a more expensive insulating material that displays one or more of the following characteristics: decreased flammability and reduced production of smoke particulates and toxic gases.

7. Silicones and polyimides (primarily film) are two classes of commercial cable-insulating materials that do not depend on halogens (either as an addition or as part of the structure of the polymer) to provide fire-resistant properties. However, they cost more than PVC and polyethylene.

Recommendations

1. Develop novel means for reducing the flammability of polyolefins without the use of halogens.

2. Determine the suitability of new PVC formulations for use as cable-insulating materials. Develop comparative data on "fire-resistant, improved" PVC formulation(s).

3. Define the problems associated with fluorine-containing polymers, for example, the toxicity of their combustion products.

4. Encourage future development of polyphosphazenes, defining advantages and problems.

5. Give increased attention to those applications where the use of more expensive materials can lead to a greater measure of safety and ultimately prove to be cost effective.

TESTING FOR FLAMMABILITY, SMOKE, AND CORROSIVE GASES

Conclusions

1. The present methods of testing for corrosivity of the various gaseous products of combustion are not entirely satisfactory. Corrosion test data on more than one metallic conductor are required.

2. The modified ASTM E-84 tunnel test was proposed as a means for simultaneously measuring both flame propagation and smoke emission. The method may be unreliable for thermoplastics. The geometry in use was not taken into account.

3. The IEEE 383 Vertical Cable Tray Test method is considered to be the best current test for simulation of fire propagation along cableways. However, further test development needs to be undertaken to evaluate the effect of such variables as heat flux, cable spacing, tray fill, corner testing.

4. The NBS Smoke Chamber is not now suitable for testing large-size cables.

Recommendations

1. Develop test methods for corrosivity of products of combustion based on the application or end use.

2. For certain specific applications, the ASTM E-84 method appears promising. However, it is limited because of an inability to handle large-size cables and because of the excessive cost of operation. Develop techniques to take into account the testing of thermoplastics and use geometry.

3. Continue to determine the efficacy of increasing the heat flux in the IEEE 383 test. Investigate cable spacing, tray fill, corner testing, and test-chamber parameters.

4. Continue the evaluation of the NBS Smoke Chamber or some other method, such as the IEEE 383, to define a smoke-test procedure for large-size cable insulations.

TOXICITY TESTING

Conclusions

1. Standardized test procedures for determining the toxicity of pyrolysis and/or combustion products of electric cable polymers are unavailable.

2. Although the state of the art in fire toxicology does not allow standardized protocols, currently available methods are capable of detecting extremely toxic pyrolysis and/or combustion products that would present an extreme hazard in a real fire situation.

3. Delayed effects of toxic products, which may be just as life-threatening as is the more immediate toxic response, require more emphasis.

Recommendations

1. Place greater emphasis on toxicity of pyrolysis and/or combustion products as a factor in the selection of wire and cable insulations.

2. Continue research on methodology in order to provide a basis for developing standardized toxicity-screening procedures for ranking materials. Place greater emphasis on delayed effects.

3. Toxicity-screening systems should be validated against large-scale tests to approximate the "real fire" situation.

DETECTION DEVICES

Conclusions

1. Despite prevention procedures, fires do occur. Ideal "nonburning" cable materials are not available and do not appear to be on the horizon. Detection methods are necessary.

2. In the design of a detection system it is necessary to assess the risk before the level of sophistication is chosen so that appropriate warning can be obtained within reasonable cost. Special hazards that place an operating

system in a particularly vulnerable position, such as submerged submarines experiencing a control cable fire, merit specially detailed detection and suppression system techniques.

3. The Navy uses large amounts of PVC for cable insulation, the pyrolysis products of which are difficult to detect with current early-warning detectors.

Recommendations

1. Emphasize the use of detection devices for early warning.

2. Develop a balanced system of detection with redundant detectors, multiplicity of types, strategic deployment, an automatic suppression system, and fire stops and other passive restraints to limit the spread of fire.

3. Develop special techniques for early detection of the products of pyrolysis of PVC.

PRESENTATIONS

FLAMMABILITY OF ELECTRIC WIRE AND CABLE INSULATIONS

Stephen B. Hamilton
General Electric Company, Bridgeport, Connecticut

The increasing use of organic polymeric materials as insulations for electric wire and cable has led to growing concern about the flammability of these insulations. Although not the most probable cause of an electrically initiated fire, cable insulations have been cited as the means for propagation of the fire from the flame source. In addition, cable insulations have been cited as a principal sources of smoke and corrosive and toxic vapors. These concerns and, more specifically, concerns about fires in naval shipboard applications, have prompted the establishment of this workshop to discuss the flammability of electric cables, including aspects of smoke, corrosion, toxicity, and flammability testing.

As an introduction to the workshop, it is the purpose of this presentation to describe cable products in general terms and to discuss, more specifically, insulation chemistry as it relates to flammability. Overviews of materials and tests that are being used in the industry, as well as some specific results developed in our laboratories, are also presented.

Electric wire and cable serve two general purposes, that is, to transmit power from one location to another, such as from an electrical generating station through various substations and transformers ultimately to buildings or equipment that consume power, and, second, to transmit a signal from one location to another to serve as a control function for all sorts of equipment.

Power and control cables are used in many applications: in power generating stations, power transmission and distribution; in industrial equipment control, transportation vehicles, communication, and construction; and for internal wiring of many industrial and consumer devices, such as household appliances, switchgear, transformers, etc.

These products range in complexity from solid-strand, single-conductor wire to multistrand, multiconductor cable employing ground wires, shields, interlocked armor, and jackets of various types. The multiplicity of designs and materials is one of the factors that necessitates large-scale flame tests of completed cables in contrast to small-scale tests of individual components.

Wire and cable products can be differentiated by their conductor types and insulation types. Conductors can be either solid or stranded for greater flexibility, and cables can consist of a single conductor or multiconductors. Conductor materials are generally either copper, or tinned copper which is used to improve strippability or solderability and to reduce corrosion. Aluminum is used mostly in the larger sizes of power cable. While conductors may be varied to meet application requirements by size or type, it is the insulation that largely determines the suitability of a cable for a particular application, and it is also the insulation that determines the flammability characteristics of the cable, which are major concerns today.

INSULATIONS

As the term implies, the prime purpose of an insulation is to insulate the conductor. This means that it must have the electrical properties required for the application, such as resistivity, resistance to breakdown, power factor, etc., and it also must be able to maintain these characteristics for long periods under conditions that might be expected in its use, such as electrical stresses, elevated temperatures, or moisture. It must also have the mechanical properties required for its installation and performance, and it must have flammability properties consistent with the application and/or the specification.

The development of insulations for wire and cable is being carried out in many laboratories, for example, by some of the large chemical companies who supply either polymers or insulation compounds to the industry. Within the industry, most wire and cable manufacturers do at least part of their own formulation work, and a few manufacturers develop most of their own insulation. This development work is now largely focused on insulations with lessened flammability, smoke particulates, and gases emitted in response to heat or flame.

Polymer insulations fall into the two general classes of thermoplastics and thermosets. Thermoplastics, as the name implies, are materials that will melt and flow under heat and pressure. Whereas they can be used as insulations per se, there is always the possibility that a runaway temperature may occur that will cause the insulation to melt and to bare the conductor, resulting in an electrical failure. This limitation must be taken into account when the use of thermoplastic materials is considered. Another limitation in the use of thermoplastics was pointed out by J. J. Garland (1) in his discussion of the development of the vertical-tray flame test for power generation stations: "The expansion of the test requirements to include circuit integrity took its toll among the suppliers of thermoplastic materials. Thermosetting compounds, which stay in place even though badly charred, fared much better on the continuity requirement than thermoplastic materials, which flow off and leave adjacent conductors bare. The flow, from thermoplastics, of hot, often flaming, particles is also a hazard."

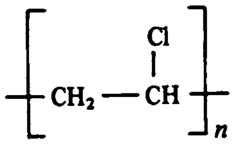
Thermoplastics may be converted into thermosets, however, by a reaction known as crosslinking, or vulcanizing. Once this is done, the thermoset material will not melt or flow as the temperature increases:

Certain materials, such as polyethylene and PVC, are used as both thermoplastic and thermoset insulations. Others, such as ethylene-propylene rubber, SBR, neoprene, Hypalon, and ethylene-vinyl acetate copolymer are used only as thermosets. There are new thermoplastic materials, such as thermoplastic elastomers, that perform very much like rubber at room temperature but of course will melt and flow at higher temperatures. There are a number of fluoropolymers available, one example of which, Teflon, behaves like a thermoset in that it does not melt at high temperatures. Another is Tefzel, which is a high-temperature thermoplastic.

From a formulation point of view, flame-resistant insulations can be separated into those that do and those that do not contain halogen. Because PVC is the flame-resistant material most commonly used in the industry, and because it contains chlorine, there has been a tendency to equate PVC and chlorine with all of the detrimental properties of halogens and halogen-containing insulations.

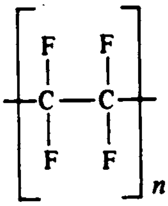
Actually, chlorine is only one of the three common halogens, which include fluorine and bromine, that are used to impart flame resistance, in many cases with an additive such as antimony oxide, which improves their performance. Among the flame-resistant insulations that do not contain halogens, only silicone produces a high-quality insulation; hydrated alumina, offered as an additive, retards burning by absorbing heat and releasing moisture, but it does not produce a high-quality insulation because of the moisture that is present. Asbestos suffers from deficient electrical properties and causes environmental problems. Since silicones frequently cost more or take up more space the common approach to flame resistance is through the use of halogens, with or without synergistic additives.

There are two basic approaches to developing flame-retardant insulations involving halogens. One of these involves having halogen attached directly to the polymer molecule, as shown in the structure of PVC and polytetrafluoroethylene (PTFE):



$$\left[-CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}H-\right]_n$$

PVC



$$\left[-\underset{\underset{\displaystyle F}{|}}{\overset{\overset{\displaystyle F}{|}}{C}}-\underset{\underset{\displaystyle F}{|}}{\overset{\overset{\displaystyle F}{|}}{C}}-\right]_n$$

PTFE

The second approach is to add a halogenated additive to a polymer such as polyethylene. There are available for use a number of highly chlorinated or brominated complex organic materials for insulation compounding: such as dechlorane, brominated biaryls, and brominated arylethers. This approach is being more and more widely used, since it offers a great opportunity for innovation and variety. It should be noted, however, that the stability of the additive in the polymer matrix must be considered. There have been cases where an insulation has the required flame resistance when it is initially produced but loses these properties later because the additive is lost owing to instability or volatility.

Some of the typical halogen-containing insulations, categorized in terms of whether they employ halogenated additives or halogenated polymers, are listed in Table 1.

TABLE 1

Typical Halogen-Containing Insulations

Polymeric	Additive
PVC (Cl)	FR - XLPE (Cl or Br)
XLPVC (Cl)	FR - EPR (Cl or Br)
Tefzel (F)	
Neoprene (Cl)	
Hypalon (Cl)	
Other fluoropolymers (F)	

FLAME TESTS

The growing realization that many factors contribute to flame test results, in ways that are often not understood, has discouraged engineers from extrapolating data from one test configuration to another. As a result, there is a proliferation of flame tests designed to simulate various application conditions. Although it is beyond the scope of this paper to review flame tests comprehensively, the vertical-tray test adopted by IEEE for nuclear generating stations in its Regulatory Guides 323 and 383 is worthy of discussion (2).

This test requires that a single layer of test cables be installed in a 12-in.-wide, 3-in.-deep, 8-ft-long vertical cable tray. The layer of cable shall at least fill the center, 6-in. portion of the tray, with a separation of approximately one half the cable diameter between each cable. The cable mounted in the vertical tray is subjected to a flame from a 10-in.-wide gas burner with a heat input of 70,000 BTU/hour, at an approximate temperature of 1500°F. The thermal output in British thermal units is a theoretical number based on the complete oxidation of propane gas to CO_2 and H_2O. The flame is applied 24 in. above the bottom of the vertical tray and 3 in. from the cable outer surface (per IEEE 383-74). The flame is allowed to burn for a period of 20 min and is then shut off. The criterion for passing is that the flame shall not propagate and burn the total of the 8-ft tray. Recently, many variations of this test have been evaluated, such as raising the burner output to 210,000 and to 400,000 Btu/hour. Tests have also been carried out with trays filled to 30 to 40 percent volume, which is near the practical limit for tray fill. This is a more important test, because it has been observed that the severity of the test increases dramatically as the number of cables increases, and trays will usually be filled to their limits in practice.

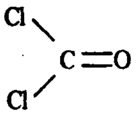
The results of some recent tests carried out at an independent testing laboratory are given in Table 2. These tests involve two types of flame-resistant insulation or jacket systems under evaluation at the General Electric Wire and Cable Laboratories, one a flame-resistant, crosslinked polyethylene cable with a neoprene rubber jacket and the other a Tefzel-insulated cable with a Tefzel jacket (3). The flame nozzle distance from the samples was based on the work of Ryan and Perkins (4), who determined the distance of maximum flame impingement on the cables. This distance was selected for these tests. The purpose of the recent work was to compare two materials approaches to flame-resistant control cable and to investigate the possibility that improper anchoring of cables at the top of the tray would be a major factor in determining flame test results. In the prior work (4), a flame test was performed involving 7C/12AWG Tefzel-insulated cables with a Tefzel jacket. The tray was loaded with 88 cables, representing a 30 percent volume fill. The cables were anchored to the top rung of the tray with metal ties. With the flame output at 210,000 Btu/hour and the nozzle distance 13 in. from the samples, the flame propagated rapidly toward the top of the rack. The thermoplastic material dripped from the cables above and appeared to feed the flame. In addition, the cables slipped from their anchors at the top of the tray and fell into the center of the fire. This latter effect was undoubtedly a contributor to the violence of the flame and the speed at which the cables were consumed. In the current test, this latter effect was prevented by wrapping the cable lengths over the top rung of the rack, and leading the end back through the interior of the tray so that a single segment accounted for two individual cable lengths.

The results (see Table 2) show that the flame-resistant XLPE cable with the neoprene jacket passed the length of burn criteria (within 8 ft) at all test conditions, including IEEE and 40 percent tray fills at both 210,000 and 400,000 Btu/hour. The Tefzel construction at a 40 percent fill passed the requirement at 210,000 Btu/hour, but when the flame was set at 400,000 Btu/hour, the cable was completely consumed by flames in the Ryan and Perkins test. In the current case, it was obvious that the thermoplastic nature of the insulation and jacket was fueling the fire from above, as the rising temperature caused the Tefzel insulation to melt and flow toward the flame.

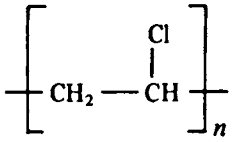
EMISSIONS

A question raised is whether or not phosgene is produced when an insulation such as PVC burns. Phosgene is a well-known, highly toxic material used in chemical warfare. The suggestion that it is formed during the burning of PVC has created considerable alarm.

Phosgene is just one member of the family of carbonyl halides, which include carbonyl chloride, carbonyl fluoride, and carbonyl bromide. As pointed out by Skinner and McNeal in their discussion of the absence of phosgene in the combustion products of neoprene (5), carbonyl chloride has two chlorine atoms attached to a single carbon atom. In the structure of PVC (neoprene is analogous) only one chlorine is attached to a single carbon atom:



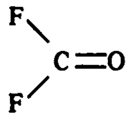
Carbonyl Chloride



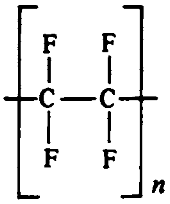
$$\left[-CH_2 - \underset{}{\overset{Cl}{\overset{|}{CH}}} - \right]_n$$

PVC

Thus, in order for carbonyl chloride to be formed from one of these polymers, a rearrangement of the basic polymer structure is required: such rearrangement may not be impossible considering the temperature of these reactions, but it is unlikely. In fact, the only case discovered where carbonyl halide was formed during the combustion of a halogen-containing polymer was that of Teflon. It was reported by Zapp (6), Waritz (7), and Fenimore and Jones (8) that when Teflon is heated in an oxidizing atmosphere, carbonyl fluoride is formed. In the structure of Teflon (PTFE), two fluorine atoms are attached to each carbon atom, just as in the structure of carbonyl fluoride, so that a rearrangement reaction is not necessary:



Carbonyl Fluoride



PTFE

Similar concerns have also been expressed that free halogens might be formed during combustion. Free halogens are more toxic and chemically reactive than are the hydrogen halides because they are strong oxidizing agents. However, for the free halogens to be formed, a chemical reduction would have to take place, which is highly unlikely in the strong oxidizing environment of a fire. Actually, no evidence has been presented in any of the papers surveyed or has been obtained in any of the work carried out in our laboratories to indicate that free halogen is a product of combustion of a halogen-containing insulation.

The data that are available regarding insulation combustion products indicate that the hydrogen halide accounts for most of the halogen present in an insulation that also contains hydrogen. For example, Boettner et al. (9) accounted for 583 mg out of a possible 584 mg of HCl gas from the decomposition of PVC polymer in air at 25° to 580°C. The remaining chloride was found as traces of methyl and vinyl chloride. Tsuchiya and Sumi (10) were able to account for 92 to 100 percent of the theoretical chloride as HCl gas when PVC was heated in helium from 350° to 850°C, and similar results were obtained by Wooley (11) in air and nitrogen atmospheres. Benbow and Cullis have similarly reported in the case of insulations containing brominated biphenyl and arylethers that more than 90 percent of the available bromine was accounted for as hydrogen bromide (12). It is this author's opinion that, were it not for sampling difficulties, a problem common to all of the above studies, the hydrogen halide recovery would have been nearly quantitative.

The production of halogen acids is not a primary result, obviously, of the combustion of insulations that do not contain hydrogen, such as Teflon. When Teflon is heated in an oxidizing atmosphere, carbon monoxide, carbonyl fluoride (which hydrolyzes rapidly to HF and CO_2 in the presence of moisture), and carbon tetrafluoride are formed to a large extent, but more complex products may be formed in smaller amounts. These products include the TFE monomer, hexafluoropropylene, and the highly toxic perfluoroisobutylene, which is formed in a small amount at 475°C (13,14).

The halogen acids are the source of the corrosive effects of burning insulations and are cited as the cause of serious pulmonary illnesses observed in fire fighters involved in PVC fires. The quantities of these acids produced in a given fire depend on the halogen content of the insulation and the amount of insulation that is burned. When considering quantities of these gases, we should think in terms of moles or gram molecular weights of these materials rather than in terms of weight per se, since the number of moles relates directly to the number of molecules of the gas produced and therefore relates directly to the volumes and chemical reactivities of these gases. For example, a gram of hydrogen fluoride has roughly 4 times the number of molecules, volume, and chemical reactivity as a gram of hydrogen bromide because of the difference in the molecular weight. The amount of halogen contained in an insulation varies widely; for example, a totally fluorinated polymer such as Teflon contains 76 percent fluorine by weight whereas PVC contains 57 percent chlorine by weight. However, after compounding PVC with fillers and plasticizers, the typical chlorine content is about 25 to 35 percent.

Table 3 gives the results of single-wire constructions subjected to the IPCEA S19-81 vertical flame test (15) in order to determine the moles of acidic gases produced from various wire constructions, based on the assumption that all the halogen consumed in the flame is converted to the acid. The samples were weighed before and after the tests, care being taken to collect any thermoplastic material that flowed away from the flame site.

Although the samples are not directly comparable in terms of wall thickness and wire gauge, the results show, for example in the extreme comparison, a construction employing 20 mils of Tefzel consumes an order of magnitude more halogen than a crosslinked polyethylene insulation employing a brominated flame retardant.

Another major concern is the amount of smoke particulates produced in a fire, since smoke can result in loss of visibility and cause confusion on the part of people attempting to exit. It has already been said that, with respect to wire and cable insulations, where there's fire,

TABLE 2 Modified IEEE-383 Flame Test

Insulation/Jacket	Construction	Cable Lengths	Volume Fill (%)	Burner Output (Btu/hour)	Burner Distance to Cables (in.)	Length of Burn (ft)	Test Results [a]
FR-XLPE/Neoprene	7C/16 AWG	106	40	400,000	20	7 3/4	Pass
FR-XLPE/Neoprene	7C/16 AWG	9	IEEE Fill	210,000	13 1/2	6 1/2	Pass
FR-XLPE/Neoprene	7C/12 AWG	52	40	210,000	13 1/2	6	Pass
FR-XLPE/Neoprene	7C/12 AWG	52	40	400,000	20	7 3/4	Pass
FR-XLPE/Neoprene	7C/12 AWG	6	IEEE Fill	210,000	13 1/2	4	Pass
Tefzel/Tefzel	7C/16 AWG	293	40	400,000	20	8	Pass
Tefzel/Tefzel	7C/16 AWG	293	40	210,000	13 1/2	6	Pass

[a] The pass-fail criterion used, which is described in IEEE-383-1974, was intended for use with a 70,000 Btu/hour flame source. Since the 70,000 Btu/hour flame test is less severe than the 210,000 or 400,000 Btu/hour tests conducted, different pass-fail criteria might be appropriate for the more stringent tests.

TABLE 3 IPCEA S19-81 Vertical Flame Test

Insulation Type	Construction Wall (mils)	Construction AWG	Length of Burn (cm)	Insulation Consumed (g)	HALOGEN % by Weight	HALOGEN Moles/lb Insulation	HALOGEN Moles/m Conductor	HALOGEN Grams Consumed	HALOGEN Moles Consumed (X 10^{-3})
FR-XLPE (Cl)	45	12	12	1.1	13 (Cl)	0.37	0.07	0.15	4.1
FR-XLPE (Br)	30	12	11	0.7	19 (Br)	0.24	0.03	0.13	1.7
XLPVC (Cl)	30	12	13	1.2	27 (Cl)	0.76	0.08	0.32	9.3
Hypalon (Cl)	60	14	11	2.1	27 (Cl)	0.76	0.21	0.57	16.0
Tefzel (F)	20	12	10	0.6	59 (F)	3.10	2.78	0.37	18.8

there's smoke. It is a source of frequent frustration that successful efforts to reduce flammability result in increased smoke-particulate production as the rate of burning is decreased. It should be noted, however, that the amount of smoke produced is highly dependent on the test conditions, and it is very likely that a material that smokes more than another at one set of exposures might smoke less than the other under different conditions favoring its more complete combustion. Therefore, a single set of test results can be misleading if one is attempting to rate materials on their tendency to smoke.

In summary then, it is important for the cable specifier to understand the insulation chemistry, particularly with respect to how the flame retardance has been developed, in order to fully understand how the cable might perform in a flame situation. It is also important to realize that a single set of flame-test results can be misleading. We have observed that insulations ranked in terms of their flame resistance at one test condition might have a different ranking if the test condition is changed. We will have a great deal to learn about these flame tests, and perhaps the pooling of knowledge that we will accomplish during this workshop will lead to a better understanding.

REFERENCES

1. J. J. Garland. Minimizing Fire Potential in Power Plant Cable Systems. Report by the Philadelphia Electric Company, prepared for NRC Conference on Electrical Insulation and Dielectric Phenomena, October 20, 1977.

2. IEEE. For Qualifying Class IE Equipment for Nuclear Power Generating Stations. IEEE Stand. 323-1974, February 28, 1974.

   IEEE. For Type Test of Class IE Electric Cables, Field Splices, and Connections for Nuclear Power Generating Stations. IEEE Stand. 323-1974, April 15, 1974.

3. S. B. Hamilton. Unpublished work, General Electric Wire and Cable Laboratories, Bridgeport, Conn., 1976-1977.

4. P. J. Ryan, Sr., and J. R. Perkins. Report on Larger Scale Cable Fires, Underwriters Laboratories, North Brook, Ill., September 27-29, 1976.

5. G. S. Skinner, and J. H. McNeal. Decomposition of elastomers at high temperature. Ind. Eng. Chem. 40:2303, December 1948.

6. J. A. Zapp, Jr. Fires, Toxicity, and Plastics. Paper presented at International Symposium on Combustion Products, National Academy of Sciences, Washington, D.C., 1976.

7. R. S. Waritz. An industrial approach to evaluation of pyrolysis and combustion hazards. Environ. Health Perspect. 11:197-202, 1975.

8. C. P. Fenimore, and G. W. Jones. Modes of inhibiting polymer flammability. Combust. Flame 10(3):295, 1966.

9. E. A. Boettner, G. Ball, and B. Weiss. Analysis of the volatile combustion products of vinyl plastics. J. Appl. Polym. Sci. 13:377-391 1969.

10. Y. Tsuchiya, and K. Sumi. Thermal Decomposition Products of Poly(vinyl chloride). J. Appl. Chem. 17:364-366, 1967.

11. W. D. Wooley. Decomposition products of PVC for studies of fire. Br. Polym. J. 3, July 1971.

12. A. W. Benbow, and C. F. Cullis. The formation of toxic products during the combustion of halogen containing polymers. Eur.Polym. J. 11:723-727, 1975.

13. V. L. Carter, D. A. Bafus, H. P. Warrington, and E. S. Harris. The acute inhalation toxicity in rats from the pyrolysis products of four fluoropolymers. Toxicol. and Appl. Pharmacol. 30:369-376,1974.

14. J. W. Clayton, Jr. Fluorocarbon toxicity and biological action. Fluorine Chem. Rev. 1:197-252, 1967.

15. IPCEA. Publication No. S-19-81 (5th ed.).

SOME FUNDAMENTAL PROBLEMS IN TOXIC HAZARD EVALUATION FOR WIRE AND CABLE INSULATIONS

John O. Punderson
E. I. DuPont de Nemours and Company, Parkersburg, West Virginia

This review is the result of a 2-year study by members of IEEE Task Group 12-36, Test Methods for Smoke, Toxicity, and Corrosive Products of Cable Combustion. Test methods for toxicity in all its aspects, including toxic effects of smoke and corrosive products, were investigated.

DEFINING THE PROBLEM

The committee sought a test method for toxicity of wire and cable insulations under conditions of fire exposure. In order to define the task more precisely, it was assumed that the suitability of such a test will be judged in terms of its usefulness in material selection for the purpose of improving human safety.

OVERCOMING COMMON MISCONCEPTIONS

It is commonly believed that some polymers are significantly "more toxic" than others. Yet when the facts are examined, we find research reports showing that highly toxic materials can be formed from a given polymer under certain laboratory conditions but no evidence as to whether or not toxic materials actually are formed in any significant amount in a fire. More importantly, such toxicity "information" is usually put forth without benefit of an equally penetrating toxicological study on any other polymer that might be considered as an alternative. The misconception here is in understanding the toxic potential from heating and burning even the simplest of organic structures.

In truth, we now recognize that all organic polymer wire insulations give off highly toxic fumes when they are heated and burned. This can be readily demonstrated by using the Approximate Lethal Temperature Test (ALT) described below.

APPROXIMATE LETHAL TEMPERATURE TEST

Although all organic polymers undergo thermal decomposition and give off toxic fumes on heating, they do not all begin decomposing at the same temperature. The minimum temperature causing onset of significant toxic emission for a given polymer can be determined by using a simple pyrolysis apparatus such as that described by Waritz and Kwon (1). A polymer sample is placed in a stainless steel pyrolysis tube and heated in a tube furnace. Air is passed through the sample tube at a controlled rate, and the exit air line is connected to an animal chamber containing six rats. A series of runs is made; typically, temperature is increased by increments of 25°C. A lethal temperature is indicated by the death of at least one rat, either during the 4-hour exposure or within 14 days after exposure. By this procedure, an ALT can be determined for any polymeric material.

For wire insulation tests it is common to wrap the wire on a smaller stainless steel tube, which is then inserted in the larger pyrolysis tube. Tests of this type were carried out on eight common wire insulations, as is listed in footnote a of Table 1. The results in the main body of Table 1 are reported in random order, concentrating attention on the pattern of performance of the group of materials rather than providing a "rating" for any particular product (2).

It will be seen that under conditions of moderate overheating for 4 hours, results varied from three out of eight insulations being lethal at 325°C to seven out of eight insulations being lethal at 400°C. For more severe short-time exposure the furnace was preheated to 705°C before the pyrolysis tube was inserted. The wire insulations were subjected to rapidly rising temperature, and all eight insulations generated fumes lethal on 12-min exposure.

Similar tests have been run on many other polymeric materials and on several common airframe wires, including two-layered constructions. All gave lethal fumes, ALT values ranging from about 230°C to somewhat over 400°C.

The ALT test provides an impressive demonstration of the fact that in spite of different chemistries and different additive systems, all organic polymer insulations produce lethal fumes.

TABLE 1 Comparison of toxicity of various wire insulations under conditions of moderate and severe overheating using ALT apparatus

	Severe		Moderate Overheating		
	Temp	705°C	400°C	350°C	325°C
Material[a]	Time	12 min	4 hours	4 hours	4 hours
A		L	L	L	L
B		L	L	O	O
C		L	L	L	L
D		L	L	L	L
E		L	L	L	O
F		L	L	O[b]	O
G		L	O	O	O
H		L	L	L	O

Procedure: Wire coated with 20 g of test material, wrapped in single layer on stainless steel tube, inserted into larger tube, and placed in preheated furnace. Air flow 3 l/min. Six rats in 20-l exposure chamber.

L = Lethal. At least one rat killed. O = Nonlethal. No deaths during exposure or within 14 days.

[a] Materials tested included PTFE, FEP, PVC, XLPVC, silicone rubber, EPR/Neoprene, EPR/Neoprene/Hypalon, and a proprietary rubber insulation, but results are presented in random order.

[b] A second specimen of this material was lethal at this condition.

The differences in ALT values for the different materials are real and reproducible. They undoubtedly have safety significance in areas of application where conditions of overheating are not too much different from those of the test itself. Current overload hazards in many situations might be predicted by this test.

The possibility of using the ALT test for fire toxicity evaluation was considered. Whether or not the ALT values would correlate with toxic hazards under real fire conditions remains an open question.

TEST METHODS--ANIMAL EXPOSURE VERSUS CHEMICAL ANALYSIS

Animal Exposure Tests

It is well known that animal exposure tests require considerable expertise and sophistication and are almost certain to be more expensive than are simple laboratory chemical analyses. For this reason, we found considerable bias favoring examination of the pros and cons of the chemical approach to toxicity prior to further examination of animal exposure tests.

Chemical Analysis and Calculations

The apparent advantages of the chemical approach can be simply stated: Chemical tests are generally cheap and quick, and it seems reasonable that use of modern analytical techniques and a great backlog of known toxicity data should give the desired toxicity comparisons.

Unfortunately, the realities of the situation do not permit this simple solution. Toxicity involves physiological response mechanisms far too complex for simple analytical prediction.

Thus, in spite of the tremendous advance in the techniques of chemical analysis and the tremendous backlog of known toxicity information, the complexities of pyrolysis chemistry and physiological response frustrate all hope of obtaining reliable results by chemical analysis and calculations.

Chemical analysis does have an important role in toxicological research when it is used in conjunction with animal exposure tests for the purpose of gaining fundamental understanding. If chemical analysis by itself is an unreliable tool for evaluation of toxicity, then toxicity judgments based on nothing but the chemical structure of the polymer must be doubly unreliable.

ANIMAL TESTS--MORE THAN ONE TYPE OF EXPERTISE NEEDED

Having found that animal tests offer the only hope for achieving valid toxicity comparisons, the committee examined the state of the art in animal testing, particularly in relation to our specific objective.

For wire insulations, the materials are not in themselves toxic. They become toxic only on exposure to fire conditions. Fire is a dynamic phenomenon covering a wide range of possible conditions, and each polymer may vary in its response to these differing conditions. The problem then is much too complex for an ordinary toxicological study, and we see that the great majority of background and experience in toxicological methods has been directed toward only part of the problem that we are attempting to resolve.

The need for more than one type of expertise is also noted in a recent paper by M. M. Birky (3). The author notes that investigations in combustion toxicity require studies on "methodology for generating the products" as well as "methodology for determining the biological response elicited from the exposure to the products."

Birky (3) further noted the work of MacFarland (4) "in which he compares conventional toxicology experiments to inhalation toxicology of combustion products. In conventional inhalation toxicity, an organism is exposed to a known quantity of a single agent, and the organism's responses are noted as a function of time and concentration. In combustion experiments, the situation is more complex. The concentration of the agent or agents is unknown and frequently the agent itself is unidentified."

Even the procedures for judging animal response to toxic exposure are not as clearly established as might be desired. Most conventional toxicological results have been expressed in terms of mortality, that is,death of test animals (usually rats). More recently, it has been suggested that in the field of fire safety, assessment of the toxic hazard causing death is not as pertinent as assessment of the toxic hazard causing loss of function, that is, loss of ability to move and escape from the zone of danger. Much recent research has been devoted to developing effective and reproducible procedures for detecting when loss of function occurs in test animals. A procedural development along these lines should provide a very positive step toward making toxicological testing more pertinent to fire safety. This research is far from complete, however, and more than one type of "end point" is being evaluated.

TOXICITY NOT AN INHERENT PROPERTY OF MATTER

Much confusion and frustration arise from the widespread practice of considering toxicity an inherent property of matter. Once this misconception is overcome, the problem becomes more manageable, for we can see what types of answers can and cannot be expected from various types of toxicity testing.

To illustrate, we are all accustomed to dealing with inherent properties of materials. We say, "Give me a test for the tensile strength of steel, and I can design a bridge," or, "Give me tests for dielectric constant and dissipation factor, and I can design a coaxial cable." If we say, "Give me a test for toxicity," we imply that toxicity is a property of matter; if this were true, it would follow that (1) materials could be rated on a scale of toxicity, (2) different materials would always remain in the same order on this toxicity scale, and (3) material specifications could call for certain limits of acceptability on the toxicity scale.

Fortunately or unfortunately, toxicity is not an inherent property of matter. Instead, toxic hazards are created by combinations of materials and conditions. This distinction may seem trivial if we are considering only conventional inhalation toxicology. Thus, we can evalute the toxicity of a gas such as carbon monoxide (CO) by fixing only one variable (exposure time) and studying animal response as a function of CO concentration. We can determine the concentration of CO causing death (or other response) in 50 percent of the test animals and obtain a fairly good assessment of the toxicity of CC. Similarly, we can test another gas such as HCN and obtain a comparison of the toxicities of CO and HCN.

In combustion toxicology, however, we encounter an enormously expanded list of variables influencing the results, and each material varies in its response to each variable. Different materials then take on differing orders of toxicity depending on conditions of combustion or heating.

TOXICITY TEST RESULTS DEPEND ON CONDITIONS

Because of the obvious complexity of conditions in real fires, most combustion toxicology studies to date have been carried out by simple heating of materials in an atmosphere of air. Even under these unrealistically simplified conditions, there are a number of variables that must be set in one manner or another, for example, amount of polymer, air-to-polymer ratio, rate of heating, temperature, exposure time, air flowing through or recirculating, etc. Several studies have shown that these variables determine not only the level of toxic hazard experienced from each test material but also the relative order of apparent toxicity among various materials.

H. Cornish (5) in a University of Michigan study reported a significant difference in order of toxicity for a number of materials tested in a "flow-through chamber" compared to the same materials tested in a "static chamber."

C. Herpol (6) of the Department of Zoophysiology, State University of Ghent, Belgium, reported results of a study on seven materials (including PVC, polyethylene, and wood) tested under three different conditions. The order of mortality produced by the materials varied markedly at each condition. PVC rates "best of seven" at one condition and "worst of seven " at another condition. Polyethylene rated among the most toxic of the seven materials under two conditions but had an intermediate position under the third condition. Analysis of these and other results led Herpol to conclude that "it appears very clearly that it is extremely difficult to produce any general conclusions at all in this kind of subject . . . it no longer makes sense to try to classify materials as "good" or "bad" according to their toxicity effects, since this behavior of a material will vary from one extreme to the other according to test conditions."

FALLACY OF ARBITRARY STANDARDIZATION OF TEST CONDITIONS

Test results are very much dependent on test conditions. Our natural impulse to seek a "reproducible test" by standardizing test conditions is tempered by the realization that an arbitrary set of test conditions will lead to an arbitrary set of toxicity ratings. Thus, it appears easy to generate reproducible test numbers but difficult to generate numbers that will have any relevance or meaning to the safety question.

It has been stated that toxicity testing might be easier if we had a "standard fire," an "IEEE fire," an "ASTM fire," or a "design basis fire." Although these concepts have been helpful in many areas, our analysis above leads to the conclusion that such standardization at this time would be premature and counterproductive to our basic desire for meaningful progress in fire safety.

THE "REAL FIRE" PROBLEM

Most real fires of any consequence are fairly large-scale events involving a range of uncontrolled conditions. It is important that we study the manner in which such fires originate, propagate, interact with materials, and create hazards. We are, however, confronted with the limitation that large-scale, real fire simulation is necessarily expensive, and, therefore, the number of experiments that can be run is limited. In addition, observation of fullscale fire phenomena does not provide as much insight as may be desired on the fundamental mechanisms of the processes involved.

On the other hand, we can see that meaningful laboratory studies on fundamental mechanisms of fire phenomena can only be pursued by fixing certain variables that range uncontrolled in real fires. No matter how these variables are fixed, the end result cannot be expected to be identical with that of any particular real fire. Laboratory results are valid for their intended purpose--to provide fundamental understanding of mechanisms of fire phenomena under controlled and specialized conditions. Such fundamental understanding has tremendous potential for long-range benefit, but in the current state of the art, laboratory research results cannot be lifted out of context to "prove" that one or another wire insulation will be "safer" in a particular end-use application.

HYPOTHETICAL ROOM-SIZED FIRE SIMULATICN

Cost has been mentioned as a deterrent to extensive large-scale fire experimentation. It is instructive to consider, however, what might be learned from even modest room-sized fire tests.

The sketch in Figure 1 represents a room-sized enclosure having a run of power or signal cable installed in a manner typical to an end-use situation of interest. A source of fire ignition is provided at one point in the cable run, and a small cage for test animals is installed at the far end of the room at the elevation of a man's head.

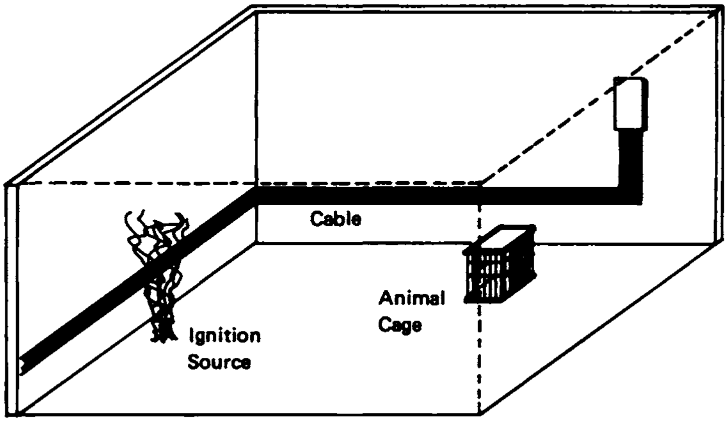
It can be expected that what happens following application of the ignition fire will be highly dependent on conditions. Some of the most important conditions are

1. air volume (or ventilation rate);
2. amount of insulation (or fuel-to-air ratio);
3. size, type, and duration of ignition source; and
4. geometry of entire setup

The potential hazards to the test animals that may develop are

1. CO (and CO_2) buildup,
2. oxygen depletion,
3. heat (temperature rise and convection of combustion products),
4. smoke (loss of visibility and panic),
5. other toxic products from insulation,
6. propagation factor, and
7. toxicity of the ignition source fire.

If the ignition source is a small fire, the events that follow may be determined by the degree to which the cable does or does not propagate the combustion. A highly nonpropagating polymer or composition may suffer only a few



CONDITIONS
1. Air volume (or ventilation rate);
2. Amount of insulation (or fuel to air ratio);
3. Size, type, and duration of ignition source; and
4. Geometry of the entire setup

HAZARDS
1. CO (and CO_2) buildup,
2. Oxygen depletion,
3. Heat (temperature rise and convection of combustion products),
4. Smoke (loss of visibility and panic),
5. Other toxic products from insulation,
6. Propagation factor,
7. Toxicity of the ignition source fire.

FIGURE 1 Hypothetical room-sized fire simulation.

grams of polymer destruction; however, a material propagating the combustion may suffer destruction of all of the insulation in the room (tens or hundreds of pounds). Because of the tremendous multiplying factor of propagation, the actual toxic hazard to the test animals may be governed more by propagation tendencies of the insulations than by the specific (per gram) toxic emissions associated with the insulations.

HAZARD OF HEAT EVOLUTION AND TEMPERATURE RISE

Preoccupation with chemical aspects of toxicity appears to have caused a general neglect of the less glamorous but perhaps equally severe hazard of heat and temperature rise in fire situations. Note in our room-sized test (Figure 1) that the heat contribution of burning wire insulation will also be influenced by the propagation factor, that is, the amount of insulation actually burned following the initial ignition.

Further, different insulation compositions vary by almost a factor of 10 in heats of combustion (British thermal units per pound of polymer burned). In addition, the weight of insulation per foot of cable varies among various constructions. All of these factors would be allowed to come into play in an actual room-sized test of the type indicated.

Heat evolution can influence toxic effects in another way not revealed by laboratory toxicity studies. Emmons (7) reports that convection caused by heat evolution is the major driving force for transport of toxic fumes from the vicinity of a fire down hallways and into nearby rooms. Certainly ,heat evolution cannot be ignored in any meaningful evaluation of toxicity hazards.

Reports of a recent full-scale fire test indicate that "plastics . . . do not seem to represent sources of increased hazard over natural materials. Neither do toxic gases, except for carbon monoxide, seem to represent primary hazards compared to the high temperature in the escape route reached within seconds of the beginning of the fire" (8).

NEED FOR TOTAL HAZARDS ASSESSMENT

Examination of the seven hazard factors listed in Figure 2 leads one to the conclusion that overemphasis on one item (specific toxic products, item 5) without due consideration of the other six factors and the interactions of these factors will almost certainly fail to provide any meaningful safety insight. At least three methods of combining the various factors to arrive at a total hazards assessment can be considered:

Simple List

Each of the known or assumed hazards is listed, and a separate evaluation is attempted for each factor. Various insulations are then compared. The difficulty is that each insulation presents a different profile of high and low ratings, and assignment of arbitrary pass-fail criteria for each property may not provide a good assessment of overall safety.

Combined Index Rating

Our attempts to evaluate fire safety of wire insulations may have much in common with similar endeavors in the field of plastics. It is our understanding that work at the National Bureau of Standards is directed toward development of a "hazard index." Properties being studied have been reported to be

1. ease of ignition,
2. smoke,
3. toxic gas emission,
4. rate of heat release,
5. flame spread, and
6. rate of burning.

It is our understanding that an attempt is being made to rate various plastics on a scale of 1 to 10 in each factor.

The overall hazard index will then be the sum of the six individual ratings. It should be noted that (1) this approach is still under study and (2) the factors measured and their relative importance will depend on the end-use situation.

Large-Scale End-Use Simulation

The only sure way to evaluate the interacting effects of the various fire hazards is to carry out some large-scale fire tests simulating typical important end-use conditions. Something similar to the room-sized setup described above might be a starting point.

COMMENT ON USUAL AND UNUSUAL TOXIC HAZARDS

Because carbon monoxide is formed to some extent in combustion of all carbon-containing materials, it is considered as a "usual" toxic hazard. Toxicologists have devoted considerable research effort toward demonstrating the presence of "unusual" toxic factors, that is, toxic combustion products giving an effect above that attributable to the CO present. In a few cases this has been successful and has indeed led to detection and identification of some previously unrecognized toxic products. This type of research is important for basic understanding.

It is also known, however, that different polymers vary considerably in the amount of CO generated under a given set of conditions and in other ways. It would, therefore, seem more logical, in the practical matter of comparative tests for material selection, to concentrate our attention on the total hazard, that is, the sum of all "usual" and "unusual" toxic factors, and on their interaction with other hazards contributing to the overall safety of the situation. If an "unusual" factor is present, let it be "weighed in" with the other hazards present.

SUMMARY AND CONCLUSIONS

At the present time there is no valid basis for selection or rejection of wire insulations based on toxicity. Some of the factors contributing to this conclusion were as follows:

1. There is no toxicity test method shown to be meaningful to fire hazards of wire insulations under use-related conditions.

2. Toxicity is not an inherent property of matter. Instead, we find that toxic hazards are created by combinations of materials and conditions.

3. Simple heating of a large group of wire insulations showed that all gave off fumes lethal to test animals. Temperatures at which the various polymers became lethal ranged from about 230°C to over 400°C.

4. The ALT has been considered as a possible toxic hazards evaluation method. Its relevance to fire hazards under end-use conditions has not been studied, however.

5. At least two other attempts to establish toxicity ratings for materials by laboratory pyrolysis methods showed that the toxicity order could be changed from one extreme to the other by changes in conditions of temperature and operating procedure. Any arbitrary set of test conditions would then be expected to give an arbitrary set of toxicity ratings.

6. Ordinarily, one might hope to establish meaningful conditions for a laboratory test method by correlation with a desired end-use result. No suitable end-use data are available, however, in this field.

7. The complexities of combustion chemistry and physiological response prevent any effective assessment of toxic hazard by chemical analysis.

8. Likewise, knowledge of chemical constitution or content of any organic polymer or insulation composition provides no valid basis for _a priori_ judgment of toxic hazard relative to other organic compositions.

9. Toxic hazard in a fire situation may be substantially more dependent on the propagation tendency of an insulation than on any specific (per gram) toxicity value. Heat of combustion may also be a major factor.

10. Consideration of the above would lead one to conclude that a specific (per gram) toxicity value (if it could be measured) would of itself provide no meaningful basis for material selection or specification. A toxic hazard assessment could become meaningful if properly combined with other hazards (propagation, heat, smoke, etc.) to arrive at an overall or total hazards evaluation.

11. The concept of "unusual" toxic hazard, useful in toxicological research, provides no basis for materials selection or specification. We can be rightfully concerned only with the sum of all toxic factors, "usual" and "unusual," and in their interaction with other hazards contributing to an overall safety assessment.

12. Large-scale fire testing under use conditions could provide a meaningful way of determining the total effect of the interacting hazards discussed above.

In view of the current state of the art, it was strongly recommended that a firm position be taken against premature and arbitrary standardization of test procedures on toxicity for use in selection of specification of wire and cable insulating materials.

REFERENCES

1. R. S. Waritz and B. K. Kwon. Am. Ind. Hyg. Assoc. J. 29:21, 1968.

2. Private communication from Haskell Laboratory of Toxicology and Industrial Medicine, E. I. Du Pont de Nemours and Company, Wilmington, Del.

3. M. M. Birky. Philosophy of testing for assessment of toxicological aspects of fire exposure. J. Combust. Toxicol. 3:5-23 1976.

4. H. N. MacFarland. The pyrolysis products of plastics--problems in defining their toxicity. Am. Ind. Hyg. Assoc. J. 29:7, 1968.

5. H. Cornish. Toxicity of Thermal-Degradation Products of Plastics. Paper presented at Symposium on Products of Combustion of Building Materials, Armstrong Cork Company, Lancaster, Pa., March 26-27, 1973.

6. C. Herpol. Biological evaluation of the toxicity of products of pyrolysis and combustion of materials. Fire and Mater. 1:29-35, 1976.

7. H. W. Emmons. Fire and Fire Protection. Sci. Am. 273:21-27, 1974.

8. W. S. Durrell, and J. H. Bateman. Chem. Technol. June:350, 1976.

FIRE TESTING OF COMMUNICATION CABLES

Stanley Kaufman (Speaker) and M. M. Yocum
Bell Laboratories, Norcross, Georgia

J. R. Beyreis and J. W. Skjordahl
Underwriters Laboratories, North Brook, Illinois

The widespread use of plastic-insulated communications cable in plenums over the past 20 years has been recognized in the National Electrical Code. As of 1975, it contained a provision that "conductors having inherent fire-resistant and low-smoke-producing characteristics approved for the purpose, shall be permitted for ducts, hollow spaces used as ducts, and plenums . . ."(1). The code stops at that point and does not define either the procedure for measuring flame and smoke properties or the acceptable levels of performance. Some localities have attempted to use existing tests and have specified minimum flame spread and smoke ratings per ASTM E-84, "The Surface Flame Spread of Materials Test." E-84 is a building materials test that is not intended to apply to cable.

This lack of standards has been a source of confusion and controversy. To an architect designing a minimum cost office building, the plenum is an attractive area to place communications cable, for it saves the expense of under-the-floor conduit (the installation method generally recommended by the telephone companies). Some localities have permitted cable installations in plenums, although others have not.

In cooperation with Bell Laboratories and manufacturers of wire and cable, Underwriters Laboratories has developed a method and a classification scheme for flame spread and smoke production of wire and cable. The test method uses the Steiner Tunnel (2) (the ASTM E-84 facility) as the test apparatus. It is similar to ASTM E-84; however, a cable rack has been introduced and the test duration is twice as long.

OBJECTIVES

Two objectives in developing a test method for communication wire and cable were:

1. to provide a numerical rank ordering of the flame spread and smoke-producing characteristics, and

2. to provide a test condition that would be meaningful with respect to actual fire conditions.

For rank ordering flame spread characteristics, it is necessary that the test specimens be sufficiently long. Quantification of smoke requires that there be a means for confining the smoke and making appropriate measurements.

For the test to be meaningful with respect to actual fire conditions, the following provisions are necessary:

1. A high heat flux characteristic of actual fires (3) (6-7 W/cm^2) is needed.

2. Large flame coverage of the test samples is needed in order to provide a high heat input to the cables.

3. The test sample should be mounted horizontally in order to simulate actual configuration in a plenum.

4. Multiple cable samples of sufficient length should be tested in order to simulate actual installation (Figure 1) and to provide a realistic amount of combustibles.

5. The test facility should be insulated in order to provide conservation of heat energy.

6. A movement of air over the test samples is needed to provide oxygen for combustion and to promote flame propagation.

7. The test must be of sufficient duration to allow the flame spread to achieve peak value.

The requirements for a test facility are met by the Steiner Tunnel, the test facility used in ASTM E-84. There are 15 Steiner Tunnels in North America. Utilization of this well-known facility has several advantages. Because it is widely used and well characterized (2, 3, 4), one has confidence in having a reproducible environment and test facility.

TEST METHOD AND CLASSIFICATION SCHEME

The fire test method for characterization of flame spread and smoke production of communications cable employs the Steiner Tunnel (Figures 2 and 3), operated in accordance with ASTM E-84 with two basic operational differences and a variation in reporting of results.

The first of the operational differences is the use of a cable rack for sample support, as is shown in Figure 3. The second difference is that the test is conducted for a 20-min period rather than the 10-min period indicated in ASTM E-84. The standard flame and draft conditions of ASTM E-84 were maintained, that is, a draft of 240 ft/min in the direction of flame growth and a 300,000-Btu/hour, 4-1/2-ft-long, methane igniting flame. The ignition source subjects the test samples to approximately 6 W/cm^2 of heat flux.

The use of a cable rack provides for total flame engulfment of the cable specimen, in contrast to the limited exposure observed in earlier tests in which the cable specimens were supported in the normal E-84 ceiling test position (5). Separation of the cable from the ceiling also provides for a reinforcement of the heating of the upper surfaces of the cable as the tunnel lid surface heats and reradiates energy to the specimen. The cable rack supports the cable high in the tunnel furnace so that it remains in the zone of maximum temperature and heat concentration. The resultant proximity of the cable specimens to the windows spaced along one wall of the furnace permits easy observation of fire development and flame spread from a close range. This test exposure mounting technique uniquely provides fire conditions that simulate the building service environment with respect to fire energy confinement, radiative feedback, large area flame coverage, and cable flame engulfment.

A 20-min test duration was chosen after it was determined that significant fire involvement of some cables

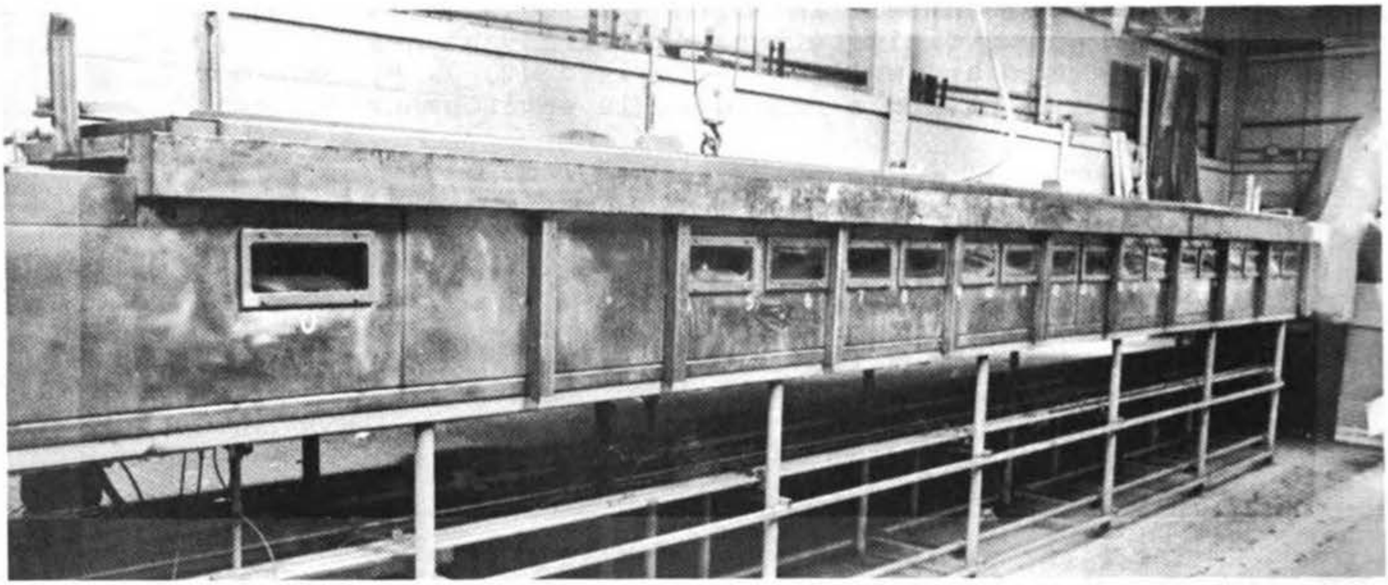


Figure 2. The Steiner Tunnel

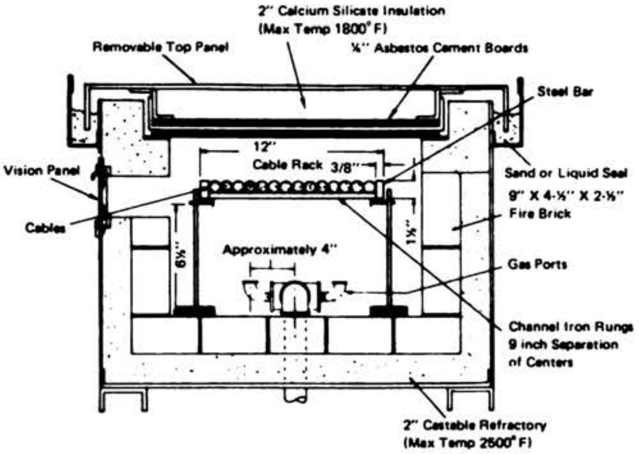


FIGURE 3 Cross section of tunnel showing mounting of cable rack.

did not occur until late in the standard 10-min E-84 test period and, in some cases, not until after the 10-min test period. In tests of 30 min or more, it became apparent that most cable constructions would reach their maximum flame spread within a 20-min test period.

A proposed classification scheme has been developed to convert the recorded test observations into flame spread and smoke-developed groupings. Because limitation of flame spread is considered the chief objective, the proposed flame spread grouping is predicated solely on distance with no credit being given to time. These groupings are:

Flame Spread Class	Flame Travel Distance, ft
I	<5
II	5-1/2 to 15
III	15-1/2 to 19-1/2
IV	>19-1/2

Class I represents a situation in which the cable ignites and burns under direct, intense exposure but fails to propagate significantly beyond the exposure fire.

Near the opposite end of the scale, cables that propagate flame in the test to near, but not past, the end of the tunnel are assigned to Class III. These cables would be recognized as having desirability of use in some occupancies where there is less hazard yet still an interest in limiting fire growth potential.

Class IV simply designates cables resulting in flame propagation beyond the end of the tunnel. The ultimate flame growth potential for such cables is unknown. Class II characterizes those cables falling between Class I and Class III.

Smoke development is monitored by a photometer system installed across the furnace exhaust duct. The photocell output is reduced as smoke passing through the duct reduces the intensity of light reaching the photocell. The output of the photocell is recorded for the 20-min test period, and the area under the resultant curve is obtained by integration over the entire 20-min test period. This area is divided by the area developed by untreated red oak lumber during a 10-min ASTM E-84 calibration test and multiplied by 100 to arrive at the smoke-developed value.

The resultant smoke values are assigned a class in accordance with the scheme:

Smoke Class	Smoke Value
A	<50
B	≥50 to ≤500
C	>500

Class A denotes a low-smoke-producing cable. Class B indicates a cable having a marked, though limited, capacity for smoke production, and Class C indicates a capacity for a high level of smoke production.

CHARACTERIZATION OF INSIDE WIRING CABLE

The test development work was carried out primarily with inside wiring cable (Figure 4). The core is made of twisted pairs of 24-gauge copper conductors insulated with 6 mils of semirigid PVC compound. Inside wiring cables do not have a core wrap or a shield. The jacket is a flexible PVC compound. Switchboard cable is of similar construction and uses identical materials.

Figure 5 shows flame spread versus time curves for five tests of 25-pair inside wiring cable. These curves are typical of well-flame-retarded cable; the flame spreads to a peak value and then recedes for the duration of the test. Figure 5 shows good test reproducibility, which has been found to be a characteristic of cables that are either very well or very poorly fire retarded.

Figure 6 shows a typical smoke curve for 25-pair cable. The smoke rating, which is calculated from the area under the smoke curve, increases with the amount of cable tested and with increasing flame spread.

Using the proposed classification scheme, these inside wiring cables are classified Class II in flame spread and Class C in smoke production.

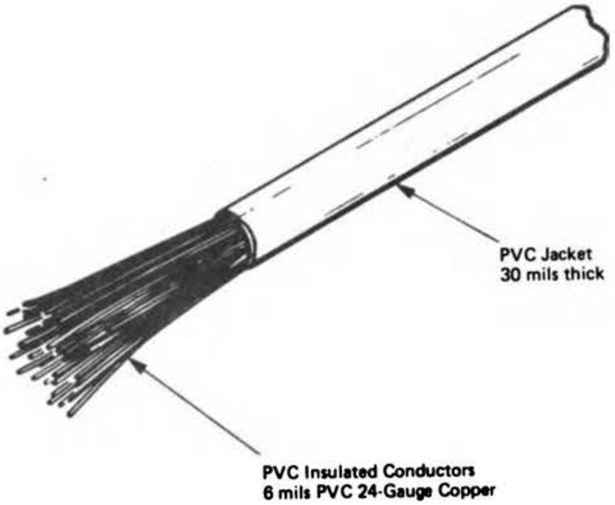


FIGURE 4 Twenty-five-pair inside wiring cable.

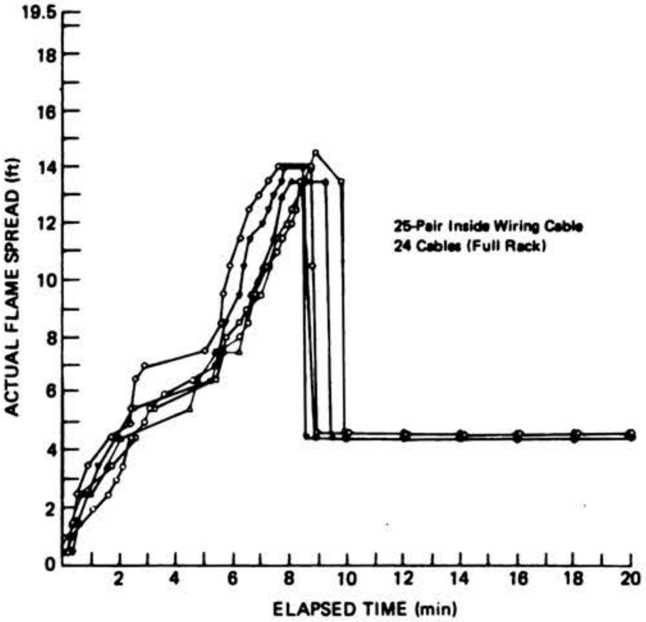


FIGURE 5 Flame spread results for five tests of 25-pair inside wiring cable.

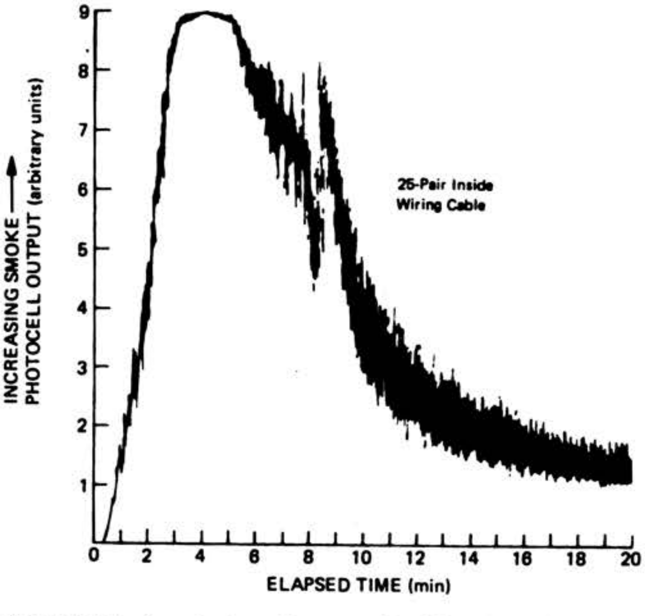


FIGURE 6 A typical smoke curve for 25-pair inside wiring cable.

CONCLUSION

The test method meets the design objectives of providing numerical values for flame spread and smoke production and therefore provides a basis for rank ordering of cables. The fire exposure conditions provided by a diffusion flame exposure, totally engulfing horizontally mounted cables under conditions of controlled airflow, are expected to be meaningful under building fire conditions where fire growth and smoke production are of concern. It is expected that the significance and limitation of the method will be explored further in large-scale fire tests.

From the Proceedings of the Twenty-fifth International Wire and Cable Symposium, Cherry Hill, N. J., November 16-18, 1976.

REFERENCES

1. National Fire Protection Association. National Electrical Code. sect. 800-3d, 1975.

2. A. J. Steiner. Fire Hazard Classification of Building Materials. UL Bull. Res. No. 32, September 1944.

3. G. T. Castino, J. R. Beyreis, and W. S. Metes. Flammability Studies of Cellular Plastics and Other Building Materials Used for Interior Finishes. UL Report, June 13, 1975.

4. L. E. Endicott, and R. B. Bowhay. A statistical evaluation of the fire hazard classification furnace (ASTM E-84-68). Mater. Res. Stand. 10(5):19, 1970.

5. S. Kaufman, and C. A. Landreth. Development of improved flame resistant interior wiring cables. In Proceedings of the Twenty-Fourth International Wire and Cable Symposium, 1975, p. 9.

THE DETECTION OF FIRE INVOLVING ELECTRIC CABLE MATERIALS

Richard G. Bright
National Bureau of Standards, Washington, D.C.

A competent fire alarm system is a key part of an overall fire protection scheme for protection of people and property. This presentation will deal specifically with the automatic detection of fire with special emphasis on the detection of fires involving electric cable materials.

LIMITATIONS OF AUTOMATIC FIRE DETECTION SYSTEMS

Automatic fire detection systems have three main drawbacks that must be considered before a decision is made to utilize these systems. First, automatic fire detection systems do nothing to prevent the outbreak of fire. Even if all fires were contained within the room of fire origin, the total fire damage would still be considerable because the frequency of fires is quite high. Second, some fires grow so rapidly, the time available for manual fire-fighting measures to be called into action by the automatic fire detection system is insufficient to prevent the fire from reaching out-of-control proportions or producing an irrecoverable loss. Third, manual fire-fighting measures are an integral part of the fire protection system also, and these need to have a response and a reliability comparable and complementary to the fire detection system. In these cases, the automatic fire detection system may need to be harnessed to an automatic extinguishing system, for example, an automatic sprinkler system.

FIRE SIGNATURES

What is it that an automatic fire detector detects? From the moment of its initiation, a hostile fire produces a variety of changes in the surrounding environment. Any product of a fire that changes the ambient conditions can be referred to as a "fire signature" (1). Some, but not all of these fire signatures are useful for automatic detection. To be useful, a fire signature should possess a measurable change, and the magnitude of this change must be greater than normal background variations. In other words, the fire signature must have a good fire signal-to-background-noise ratio. All other factors being equal, the preferred fire signature will be that which can generate the highest signal-to-noise ratio in the earliest period of fire development. In addition, the best signatures are those associated exclusively with fire in a wide variety of fuels.

Fire signatures can be grouped into three broad categories. These are:

1) aerosol signatures, such as smoke;

2) energy release signatures, such as flame and heat; and

3) gas signatures, such as CO and CO_2.

AEROSOL SIGNATURES

A fire releases a very large number of solid and liquid particles ranging in size from below 0.01 μm to perhaps 10 μm and larger. Suspensions of these particles in air are called aerosols. The class of automatic fire detectors responding to aerosols are called smoke detectors.

Nonvisible aerosols are one of the earliest appearing fire signatures noted to date. These aerosols are usually produced by the external heating of materials during the preignition stage of a fire. An example of such a pre-fire condition is the evolution of particles (condensed vapor) from the painted surfaces of an electric motor undergoing an overheat condition.

Another type of aerosol-producing fire is the smoldering fire. This fire is usually caused by a very hot object in contact with a material that, when ignited, can sustain smoldering independently of the ignition source. The classic example of this fire start is the accidental contact of a lighted cigarette with cotton upholstery materials. The aerosol particles from a smoldering fire tend to include particles in the visible region, that is, larger in size. Finally, there is the flaming fire, characterized by the presence of visible flames. A flaming fire may produce very little visible smoke. An example is a wood fire in a fireplace. This fire does, however, produce a large quantity of nonvisible species. Other flaming fires, such as those involving some of the plastics and flammable liquids, or incompletely burning wood or paper, can produce copious quantities of visible smoke, predominantly black in color. These fires produce large quantities of nonvisible species as well.

ENERGY RELEASE SIGNATURES

Throughout its course, a fire is constantly releasing energy. This energy produces several useful signatures. One such signature is the flame radiation. The fire detectors responding to this signature are the flame detectors. Flame detectors, because of their high cost and false-alarm tendency due to nonhostile radiation sources, are usually relegated to the protection of very special risks, for example, aircraft in high-bay hangars.

Another useful energy-release signature is the thermal energy given off by a fire and often referred to as heat. The heat from a fire raises the air temperature in the vicinity of the fire. The time required for the buildup of detectable heat levels can vary from less than a minute for rapidly developing fires to several hours for slowly developing or smoldering fires. In comparison to smoke and flame signatures, heat signatures can appear well after life-threatening conditions have been reached from excessive smoke or toxic-gas concentrations. For the protection of property, however, these considerations may be less important. The class of fire detectors responding to heat signatures are called heat detectors.

GAS SIGNATURES

During a fire many changes occur in the gas content of the surrounding atmosphere. For the most part, these changes consist of the addition of gaseous products to the air, gases that are not normally present in significant quantities. Many gases and vapors may be evolved during a fire. Some examples are H_2O, CO, CO_2, HCl, HCN, HF, H_2S, NH_3, NO_2, and assorted hydrocarbons. Three products are common to practically every fire: H_2O, CO, and CO_2. And of these three, CO offers the best possibility for fire-detection application. But, although this is true, it should be noted that the detection of fire using CO, or any gas signature, is in its infancy. Most, but not all, of the classes of automatic fire detectors have been mentioned. The following list summarizes nearly all of the common types of fire detectors presently available, including those already mentioned:

Heat

- Fixed temperature
- Rate of rise
- Combination of above
- Laser beam

Smoke

- Photoelectric (light scattering)
- Photoelectric (absorption/extinction)
- Ion chamber
- Extinction beam
- Cloud chamber
- Laser beam
- Fuel cell
- Hydrocarbon (combustible gas)

Radiation

- Infrared
- Ultraviolet
- Combination of above

SMOKE DETECTORS

The combustion aerosol, commonly called smoke, composed of particles ranging in size from below those which are visible to those readily visible under ordinary light, is what smoke detectors detect. This applies to both the ionization chamber smoke detector as well as the photoelectric smoke detector, the two types of smoke detectors most readily available today. These smoke detectors, particularly the ion chambers, sense some gases, but neither type of detector does this as well as for sensing particles. Therefore, both types of smoke detectors can be thought of as particle detectors or, to be more precise, as particle counters. Depending on the alarm response set point, these detectors produce an alarm when a certain number of particles are present within their sensing chambers. This particle-counting ability of the smoke detectors is complicated by the fact that the particle diameter also influences their response. And, in the case of the photoelectric smoke detectors, the wavelength of the light used in the detectors as well as the complex index of refraction of the smoke particles also influence their response.

Both the ion chamber and the photoelectric smoke detector can be made so sensitive that they can be used as air quality indicators. For instance, an ion chamber detector has been developed that can sense the difference in air quality when the eleventh person lights a cigarette in a conference room where 10 persons are already smoking. Similarly, a photoelectric detector has been developed that can sense the difference in air quality between a visibility of 120 km and that of 130 km. Obviously, this sensitivity is far too great for ordinary fire detection because of related false alarm problems. But this sensitivity might be useful, for example, if the output data from the detectors were supplied in analog fashion and this analog data were used to effect various levels and kinds of response as each succeeding, and higher, level of analog signal was reached. One possible use might be as a monitor for early breakdown conditions in electronic gear such as computers. Another possible use might be in the monitoring of the return air in a heating, ventilating, and air conditioning (HVAC) system for the detection of fires, even quite small ones, somewhere in the space served by the HVAC system. For those not familiar with these two types of smoke detectors, a short description of their operational characteristics follows.

IONIZATION CHAMBER SMOKE DETECTORS

The ion chamber responds to both visible and nonvisible smoke particles, over a size range from about 0.01 μm up to about 1.0 μm. The basic detection mechanism may be thought of as a parallel plate condenser with a voltage potential applied across the plates. A radiation source is placed between the plates. The radiation source ionizes the air molecules between the plates, an extremely small current flow between the plates resulting. When smoke particles enter the ionized air space, the particles capture some fraction of the ions, a reduction in the current flow resulting. The reduction in current flow is used to trigger the alarm circuit.

PHOTOELECTRIC SMOKE DETECTORS

Smoke particles have two effects on light that are utilized by photoelectric smoke detectors. One is the absorption of light by dark particles, and the other is the scattering of light from the straight path. In the first case, the presence of smoke particles reduces the amount of light transmitted along the path of the direct beam. This effect is known as the extinction effect. This effect is utilized in an absorption-type device for detection by placing a photoreceiver at some distance from a light source and using suitable electronics to look for the reduction in light reaching the photoreceiver. For very low smoke concentrations, fairly long path lengths are necessary to get a good signal-to-noise ratio; the longer the path length the better. At the present time, there is only one fire detection system on the market utilizing light extinction for detection, although many are used for measuring smoke in flues, chimneys, etc. This is perhaps unfortunate, for such a system has much to offer as a fire detection method.

In the second type of detector, the scattered light can be detected and measured by a photoreceiver placed at an angle to the directly transmitted light beam. This type is, by far, the more common photoelectric-type smoke detector. The photoreceiver may be placed at any angle to the light beam. But, in actual practice, it has been placed either at 90° to the beam or forward of 90° to where the photoreceiver is looking at the scattered light from the smoke particles in the forward direction. Either position will work, but the further into forward scatter the photoreceiver is placed, the better the signal-to-noise ratio. For black smokes, such as those from free-burning plastics, a forward-scatter placement of the photoreceiver is especially helpful because black smoke particles scatter much less light than do white smoke particles. Photoelectric smoke detectors work best on particle sizes from about 0.3 μm up. Below 0.3 μm, there is a sharp reduction in the light-scattering efficiency of particles.

ADVANTAGES AND DISADVANTAGES OF SMOKE DETECTORS

What are some of the advantages and disadvantages of smoke detectors in general and the ion chamber and photoelectric smoke detectors in particular? As a class, smoke detectors have a major advantage over heat detectors, in that smoke detectors are usually quicker in responding to a hostile fire, particularly if the fire produces little heat, as would be the case with a smoldering fire. However, this advantage over heat detectors is accompanied by an increase in false alarm possibilities. Table 1 [from Fry (2)] shows a comparison of false alarm ratios for all types of fire detection and protection equipment that are part of a system. In this study, a false alarm was defined as any alarm arising from other than a real fire. Notice that the overall ratio for heat detector systems is 11 to 1 and for smoke detectors, 14 to 1. The reason for the higher false alarm potential of smoke detectors over heat detectors is related to the more sensitive response of smoke detectors to all types of combustion products. As a general rule, it can be stated that the more sensitive a detector is to a given fire, the more likely the detector is to be fooled by nonfire conditions. Unfortunately, there are many processes that take place in a building each day that produce combustion-like phenomena that detectors of all types have difficulty ignoring. Table 2 shows the reasons for the false alarms. Table 3 gives the same data broken down by detector type.

TABLE 1 Behavior of Automatic Fire Alarm Systems: Ratio of False Alarms to Real Alarms

Type of System	Calls Received Fire	 False	Ratio of False to Real
Heat	193	2,146	11:1
Smoke	101	1,429	14:1
Heat and smoke	18	410	23:1
Sprinkler	101	1,048	10:1

SOURCE: British Fire Research Station.

TABLE 2 Behavior of Automatic Fire Alarm Systems: Reasons for False Alarms

Reasons for False Alarms	Percent
Ambient conditions	25.9
Mechanical and electrical	46.1
Testing, maintenance, etc.	16.6
Not specified/unknown	11.4

SOURCE: British Fire Research Station.

TABLE 3 Behavior of Automatic Fire Alarm Systems: Reasons for False Calls

Reason for False Alarms	Percent			
	Heat	Smoke	Heat/Smoke	Sprinkler
Ambient conditions	26.1	44.2	33.4	5.2
Mechanical and electrical	43.4	35.8	43.7	66.3
Testing, maintenance, etc.	18.3	11.1	11.0	21.7
Not specified/unknown	12.2	8.9	11.9	6.8

SOURCE: British Fire Research Station.

With regard to the detection of fires, ion chambers respond more quickly, as a rule, to flaming fires than do photoelectric detectors. The less visible smoke produced, the more pronounced the difference. With smoldering fires, those fires from which there may be smoke but no flaming, the photoelectric detectors, as a class, are quicker to respond than are ion chambers. Both of the above generalizations have exceptions, however. Some of the newer photoelectric detectors use what we call open optics as well as fast-responding photoreceivers. This enhances their response to low orders of smoke. As a consequence, they tend to respond rather quickly to even relatively clean-burning fires. Although many of the ion chambers exhibit slower response to smoldering fires than do photoelectric detectors, some do not. Recent tests conducted by Consumers Union on residential smoke detectors provide examples of this (3, 4). Two of the nine ion chamber detectors tested gave responses equivalent to the photoelectric detectors on smoldering fires. It is likely that the commercial versions of these same detectors, where such exist, will give similar performances.

DETECTOR RELIABILITY

One can separate the long-term performance of a detection system into two components. The first relates to the operational readiness of the sytem as a whole. Applying heat to a heat detector or smoke to a smoke detector and determining whether the system operates checks this feature. The second, much more subtle component, is the question of whether there has been a shift in the sensitivity of the sytem's detectors with time. In other words, does it take more or less heat and more or less smoke to operate the smoke detector than was required at installation? Usually, if it takes less, one can tell. But if it takes more, or if the detectors have lost sensitivity, it is not always possible to tell without removing the detectors and sending them to the laboratory for retest. All-in-all, the effective reliability of an automatic fire detection system can be improved by periodic testing and maintenance. This should be a must, but it is not always done.

With regard to the two types of smoke detectors, the passage of time generally results in the ion chamber detector becoming more sensitive and the photoelectric detector becoming less sensitive. This is not always true, however. At present, there is an ion chamber on the U.S. market that has shown an inclination to lose sensitivity with time. With photoelectric detectors, the careful design and use of compensation circuits can reduce shifts toward insensitivity.

DETECTION OF EARLY PYROLYSIS PRODUCTS FROM ELECTRIC CABLE MATERIALS

The evolution of particles from the painted surfaces of a motor undergoing an overheat condition is an example of a material undergoing pyrolysis. Pyrolysis is the chemical decomposition of a material by heat (generally in the absence of flame). Thermal degradation is often used as a synonym for pyrolysis but, only pyrolysis will be used in this presentation. While smoldering and flaming combustion are important phenomena in terms of fire detection, the following discussion will be restricted to pyrolysis and its detectability. However, there is a great similarity between pyrolysis and smoldering from a detectability standpoint. The class of fire sensors responding best to early pyrolysis products from electrical cabling materials are the smoke detectors. But, in some instances, these detectors are not as sensitive to these pyrolysis products as one might like.

The dielectric insulation materials used for cable include, among others, PVC, polyethylene, rubber, polychloroprene, and Teflon. Pyrolytic degradation of these materials is characteristically due to elevated temperatures resulting from an overload condition.

The most common electrical insulation, at least as far as the civilian sector is concerned, is PVC. This is perhaps unfortunate because the early pyrolysis products from PVC are the most difficult to detect with the presently available fire sensors, including the smoke detectors. Figure 1, from Purt (5), shows the effect of an electrical overload of 300 percent over the nominal current in a 1.5-mm^2 PVC-insulated cable. The PVC is undergoing a slow degradation accompanied by a slow weight loss. The weight loss is due, essentially, to the generation of hydrogen chloride (HCl). In the presence of atmospheric moisture, the HCl condenses, forming a pure HCl and water aerosol droplet. This generation of HCl occurs before the generation of significant quantities of carbon particles. According to Hosemann (6), neither the ionization chamber smoke detector nor the photoelectric smoke detector are able to detect this HCl aerosol. This point tends to be supported by Purt, as is shown by the bottom curve in Figure 2. Hosemann proposes other methods of detecting this HCl aerosol not based on fire sensor technology.

As the overload is increased, detection of the pyrolysis products by conventional smoke detectors becomes practical. This is shown by the three upper curves on Figure 2, the curves for the 3.75, 4, and 5 times nominal current. According to Tsuchiya and Sumi (7), the reason for the detectability of the PVC pyrolysis products above 300° to 325°C is that the carbon skeleton of the PVC becomes broken and sufficient detectable "smoke particles" form.

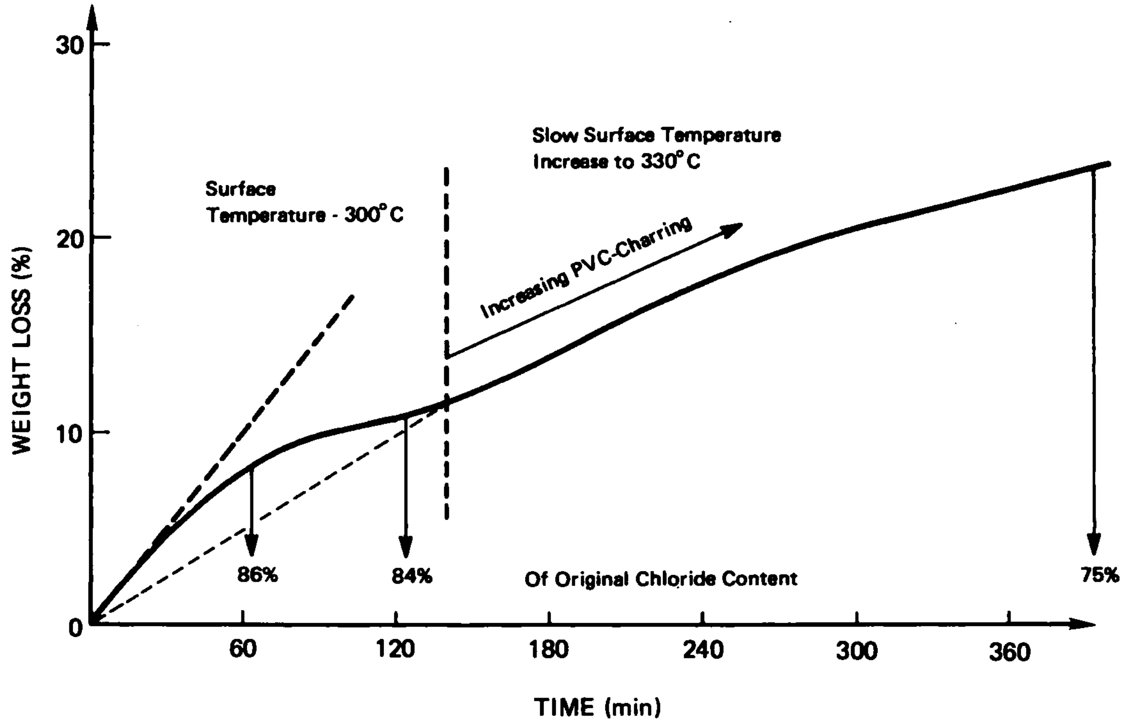


FIGURE 1 Weight loss of PVC insulation for 1.5-mm^2 cables at 3 X nominal current (45 A).

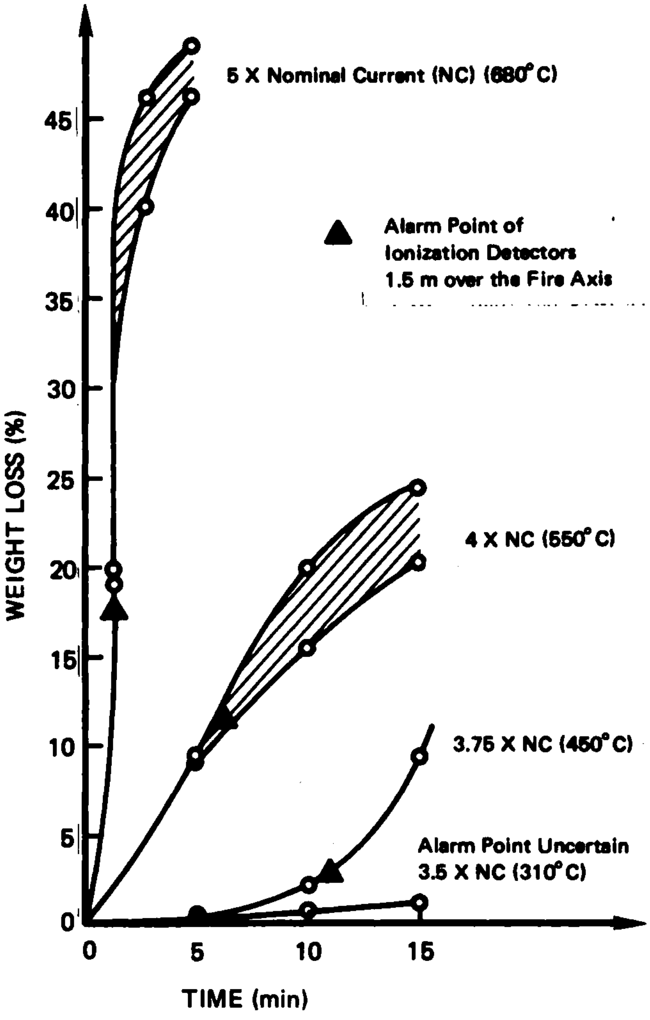


FIGURE 2 Weight loss of PVC insulation for 1-mm² cables under overload (nominal current = 10 A).

Recently, Japanese researchers reported on a series of fire tests in a computer (8). The purpose of the tests was to determine (1) the effect of fire development on data processing, (2) the possibility of very early fire detection before error occurrence or irrecoverable damage, (3) the effect of thermal shock due to discharge of the extinguishing gas on an operating computer, and (4) the toxicity and corrosiveness of combustion products, including thermal decomposition products of the extinguishing agent, Halon 1301.

Fires were started in a dummy unit, within an operating central processing unit (CPU), under the raised floor, and in the room itself. An air conditioning unit took air from the room at the ceiling, recirculated the air through the underfloor plenum and up through the equipment at 1 m/sec, and discharged the air back into the room. An ion chamber smoke detector, a photoelectric smoke detector, and a combustible gas detector were placed in the equipment, under the floor, and on the ceiling in the center of the room. The dummy unit was exposed to five fires consisting of either an overheated resistor or a nichrome wire, both on glass/epoxy boards. The CPU was exposed to nine fires consisting of an overheated resistor on a printed circuit board or a nichrome wire on a glass/epoxy board. Three underfloor fires were conducted by heating a 0.65-mm^2, PVC-covered wire with a current of 20 A. The fires in the CPU were conducted with the CPU performing a predetermined calculation process to check for the occurrence of errors.

Table 4 shows the percentage of success for each type of detector for the two types of fires of interest and for three detector locations. The percentage of success for the "All Fires" categories includes all the fire tests conducted, although only "Equipment Fires" and "Underfloor Fires" are tabulated because of their immediate interest to this discussion. From the results, the report concluded that:

1. The photoelectric detectors in the equipment had the highest overall success rate. The ionization detector showed less sensitivity because most of the test fires were smoldering. The gas sensor within the CPU showed good sensitivity, but at other positions the gas sensor's success was poor.

2. The success rate for both the photoelectric and ion chamber detectors mounted in the CPU was 60 percent for fires originating in the equipment.

TABLE 4

JAPANESE COMPUTER FIRE TESTS SUCCESS PERCENTAGES

DETECTOR LOCATIONS

		INSIDE MACHINE			UNDER FLOOR			ON CEILING		
		I	P	G	I	P	G	I	P	G
FIRE LOCATIONS	EQUIPMENT FIRES	60	60	50	30	10	10	40	30	10
	UNDERFLOOR FIRES	0	100	75	100	100	50	25	100	0
	ALL FIRES	37	79	58	63	42	26	53	63	32

NOTE: I, P, G, ARE IONIZATION, PHOTOELECTRIC & GAS DETECTORS

3. For PVC fires under the raised floor (and with the air conditioning in operation), not only the detectors under the raised floor, but also the photoelectric detectors inside the equipment and on the ceiling, responded well. Thus, detectors under the raised floor may not be necessary if one of the other two positions are available. The ionization detectors inside the CPU were completely ineffective in detecting these fires.

4. There was only one case in which the CPU printed an error. This was one of the tests with an overheated resistor on a printed circuit board. If more sensitive detectors were used, earlier detection could have been expected, and in the case of this one error occurrence, an alarm would have been given 40 sec before the error occurrence.

It should be pointed out that in most of these tests, extinguishing agents, using either CO_2 or Halon 1301, were applied after the alarms were given, though the precise timing of this action is not clear. The operating CPU was not affected by the extinguishment, although in the case of the CO_2, the CPU was subjected to a thermal shock.

While the results of the Japanese study show that detection of electrical fires in both the computer equipment and the underfloor cables was possible with conventional photoelectric smoke detectors and with the combustible gas detectors, it is not clear whether this detection success constituted true early warning. It probably did not in the sense in which the term is being used in this paper. In addition, the detectors used by the Japanese were not set at the maximum sensitivity available under their approval procedures.

Wagner and Welker have shown that ionization chamber smoke detectors are not particularly responsive to early pyrolysis products of polyethylene, polyurethane, and PVC (9, 10). They had better success with photoelectric smoke detectors than with the ion chamber detectors. The conclusion one might reach from all of this is that for the very early detection of the pyrolysis products from cable insulation materials, fire sensors operating on the photoelectric principle are to be preferred.

The cloud chamber smoke detector (11, 12, 13) is an adaptation of a laboratory condensation nuclei counter for fire detection. (See Figure 3.) An air sample containing particles to be detected is drawn through the instrument by

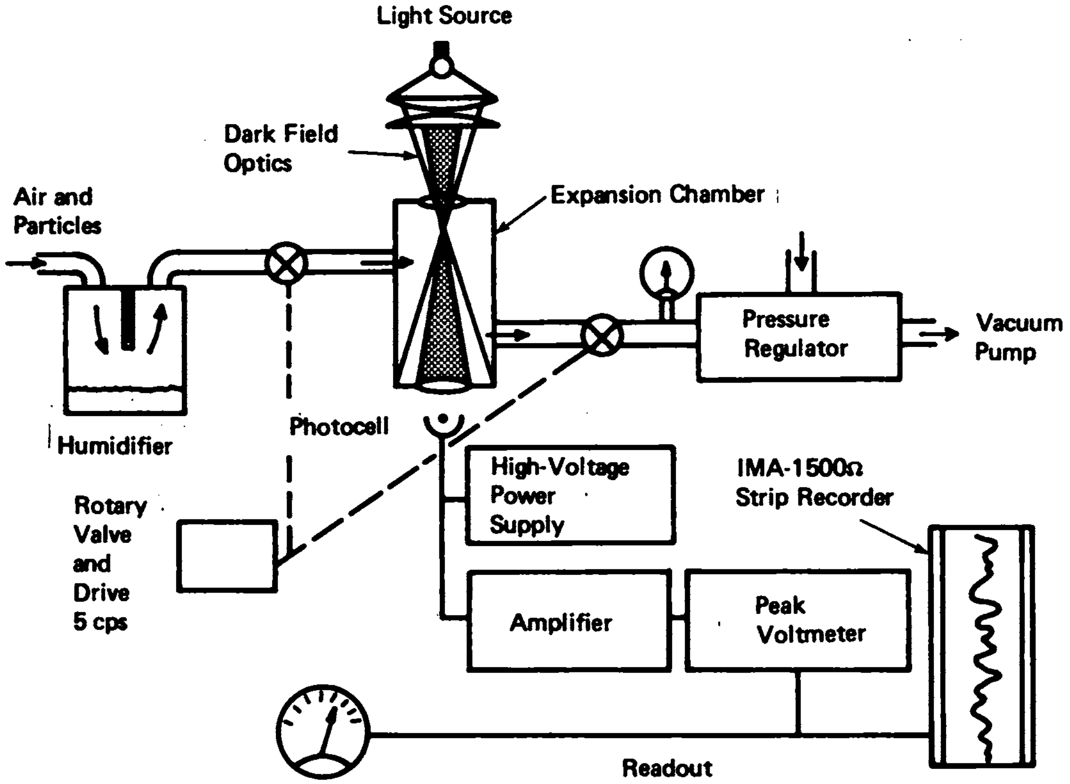


FIGURE 3 Schematic of condensation nuclei particle detector.

a vacuum pump. The sample first enters a humidifier, where its relative humidity is raised to 100 percent with water. The sample then passes into a cloud chamber, where it is expanded adiabatically, causing the sample to cool. This results in condensation on the airborne particles producing a cloud of visible water droplets. These droplets are measured in a dark-field optical system by the scattering of light off the droplets into a photomultiplier tube. The amount of light scattered is proportional to the number of droplets in the sample.

The cloud chamber smoke detector is capable of extreme sensitivity to combustion nuclei. However, there is little information available as to its field experience and performance. All-in-all, the cloud chamber smoke detector offers, at least in principle, one of the best detection possibilities for the very early warning of pyrolysis products from electrical cable materials.

There is little or no information available in the literature on the sensitivity of conventional smoke detectors to early pyrolysis products from cable materials under real world conditions. Nearly all of the information presented here is synthesized from experimental data that do not directly address the subject. In regard to early warning systems, further research is necessary to determine the specific capabilities of the available sensors in detecting pyrolysis products from cable materials.

Sensors warranting investigation include high-sensitivity photoelectric smoke detectors with open chambers and fast-responding optics, now commercially available, and the cloud chamber smoke detector. In experiments, insulating materials in general use should be subjected to the faults characteristic of the more frequently occurring, electrical problems. Through carefully conducted laboratory experimentation, it should be possible to determine which sensors, under what conditions, offer the best solution to the very early detection of pyrolysis products from cable-insulating materials.

REFERENCES

1. R. L. P. Custer, and R. G. Bright. Fire detection: The state-of-the-art. Nat. Bur. Stand. Tech. Note 839, June 1974.

2. J. F. Fry, and C. Eveleigh. The Behavior of Automatic Fire Detection Systems. Current Paper, CP 32/75, Building Research Establishment, Garston, Watford, WD2 7JR, England, April 1975.

3. Smoke detectors. Consum. Rep. 41(10):555-559, October 1976.

4. Update: Smoke detectors. Consum. Rep. 42(5):283, May 1977.

5. G. Purt. Fire Risks and Fire Protection in Connection with PVC Fires. Paper presented at Stydol Symposium, Stockholm, Swed., 1969. (Author's address: Cerberus, CH-8708 Mannedorf, Switzerland.)

6. J. P. Hosemann. Some principles of detectors for the automatic detection of HCl aerosols. Brandschutz 27(7), 1969. (In German; English translation available from author of this paper.)

7. Y. Tsuchiya, and K. Sumi. Thermal decomposition products of poly(vinyl chloride). J. Appl. Chem. 17, December 1967.

8. Joint Group on Computer Fire Protection. Report of computer fire tests. J. Jap. Assoc. Fire Sci. Eng. 24(3), 1974. (In Japanese; English translation available from author of this paper.)

9. J. P. Wagner, M. May, and A. Fookson. Comparative performance of ionization versus photoelectric fire detectors--pyrolytic degradation products. J. Fire Flammability 6, October 1975.

10. R. W. Welker, and J. P. Wagner. Particle size and mass distribution of selected smokes, Effect on ionization detector response. J. Fire Flammability 8, January 1977.

11. F. W. Van Luik. Characteristics of invisible particles generated by precombustion and combustion. Fire Technol. 10(2), May 1974.

12. F. A. Ludewig. New concept for fire detection. Fire J. 69(4), July 1975.

13. F. A. Ludewig. Application of cloud chamber techniques to fire detection. In Proceedings of a Symposium on Fire Detection for Life Safety, National Academy of Sciences/National Research Council, Washington, D. C., 1977.

ADVANCED DIELECTRIC MATERIALS:
FLUOROPOLYMERS AND POLYIMIDES

Peter N. Plimmer (Speaker) and John O. Punderson
E. I. DuPont de Nemours and Company, Parkersburg, West Virginia

FLUOROPOLYMERS

This review covers four major members of the commercial fluoropolymer family, each one developed to satisfy a specific need either in processing or in end-use performance (Figure 1). These are fully described in references (1) through (5).

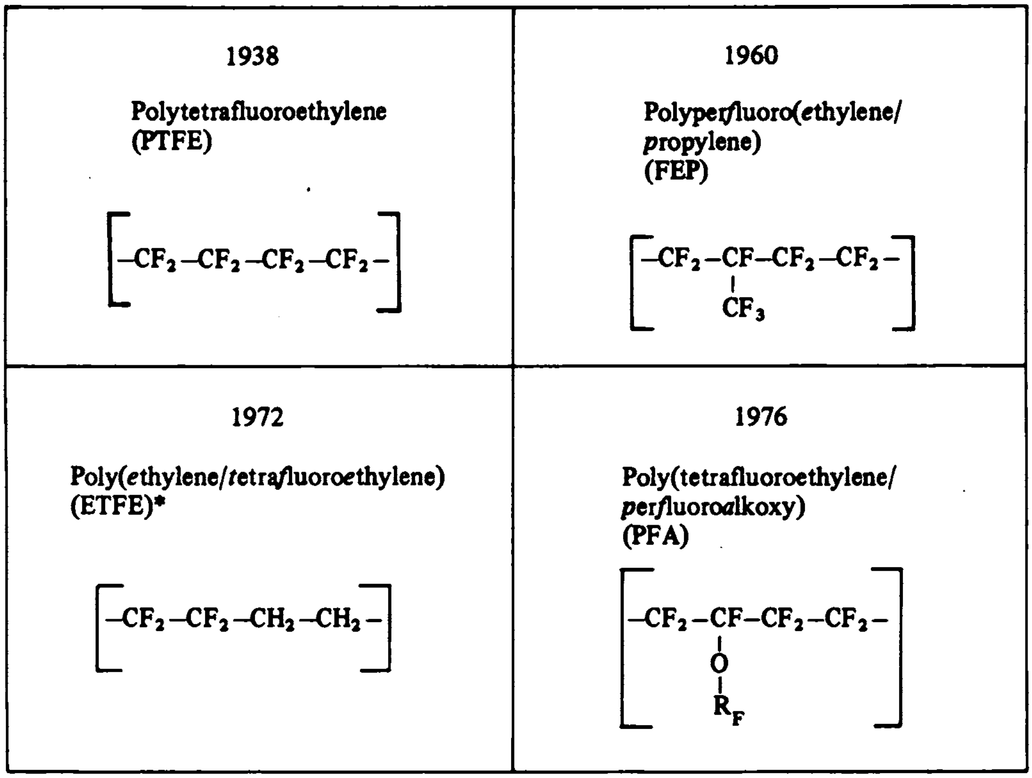
Polytetrafluoroethylene (PTFE)

Thermal Stablility and Melting Behavior

The original member of this family, PTFE, is a straight-chain, fully fluorinated polymer, discovered quite accidentally in 1938 in DuPont's laboratories by Dr. Roy Plunkett. Since that time, PTFE has become available from several sources throughout the world. This nonmelt-processible polymer has a unique combination of dielectric, chemical, and thermal properties that makes it highly desirable for use as a wire insulation. It is this combination of properties that we have strived to maintain as we have continued to develop high-performance, melt-fabricable, fluorocarbon polymers.

In order to explain the unique property profile exhibited by the fluorocarbon polymers, it is necessary to understand how the elements of the polymer molecule are chemically bonded together.

FIGURE 1 The fluoropolymer family.



$$\left[-CF_2-CF_2-CF_2-CF_2-\right]$$

$$\left[-CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-CF_2-CF_2-\right]$$

$$\left[-CF_2-CF_2-CH_2-CH_2-\right]$$

$$\left[-CF_2-\underset{\displaystyle R_F}{\underset{|}{\underset{\displaystyle O}{\underset{|}{CF}}}}-CF_2-CF_2-\right]$$

*Poly(ethylene/chlorotrifluoroethylene) ECTFE available.

PTFE, like all materials, is held together by a combination of strong primary chemical bonds and weaker secondary physical bonds. Unlike hydrocarbons, in which the C-H bond strength is less than 100 kcal/mol, the C-F bond strength in PTFE is about 115 kcal/mol, which accounts for the high degree of thermal stability of the polymer. At the other extreme, the interchain bonds (which contribute significantly to such fundamental properties as mechanical strength and melting point) are weaker than those of the hydrocarbons because, in the absence of dipoles and hydrogen bonding, the interchain forces are mainly of the short-range, van der Waals type.

This difference in thermal stability (bond strength) between hydrocarbon polymers and PTFE is reflected in the observed difference in weight loss versus temperature. For example, about a 50 percent weight loss occurs in a standard heating period for polymethylene at about 405°C, whereas for PTFE this weight loss is observed at 510°C (Figure 2). A practical implication of this inherent thermal stability lies in the ability of PTFE wire insulation to withstand direct contact with heated surfaces such as those encountered in jet engines or with soldering irons during in-place repair of electronic circuitry. In contrast, the weak interchain bonding forces mentioned above account for the low melting points of very low molecular weight tetrafluoroethylene polymers. These melting points are even lower than those of the ethylene polymers at the same molecular weight level (Figure 3).

At higher molecular weights (probably several million), however, the "melting point" of the PTFE rises sharply above the level of the polyethylene series, reflecting the cumulative benefits of these weak interchain bonds in a very high molecular weight chain. Another unusual characteristic of the high molecular weight PTFE polymer molecule--an inherent stiffness--also contributes to the peculiar nonmelting behavior of PTFE (which at 327°C has about the same viscosity as that of lead at 25°C).

This inherent stiffness can best be seen with the help of a molecular model of PTFE relative to one of polyethylene (Figure 4). Because of the size of the fluorine atom, the PTFE chain is forced to assume a helical configuration, unlike the planar zigzag of the polyethylene. This steric hindrance imparts a chain stiffness to the PTFE molecule that lowers the entropy of melting and leads to the observed high "melting point" of commercially available, high-molecular-weight PTFE.

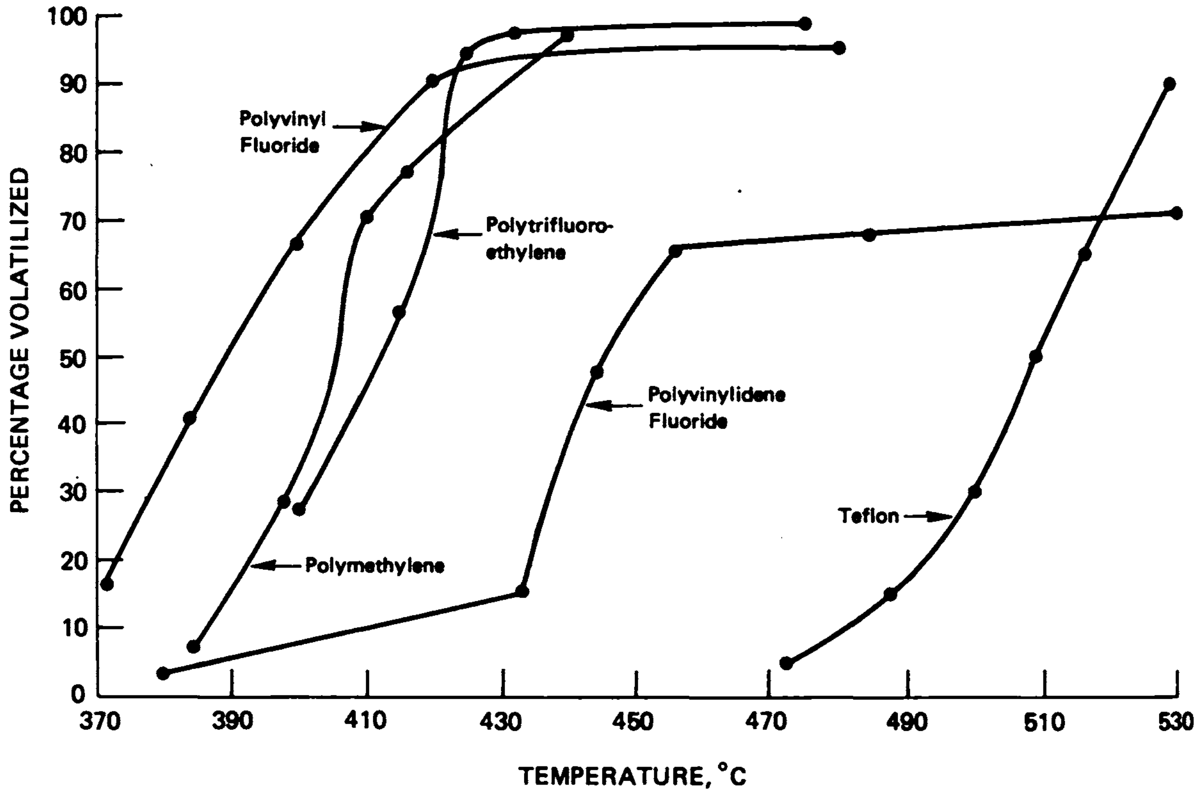


FIGURE 2 Relative thermal stability of Teflon, polymethylene, and hydrofluoroethylene polymers.

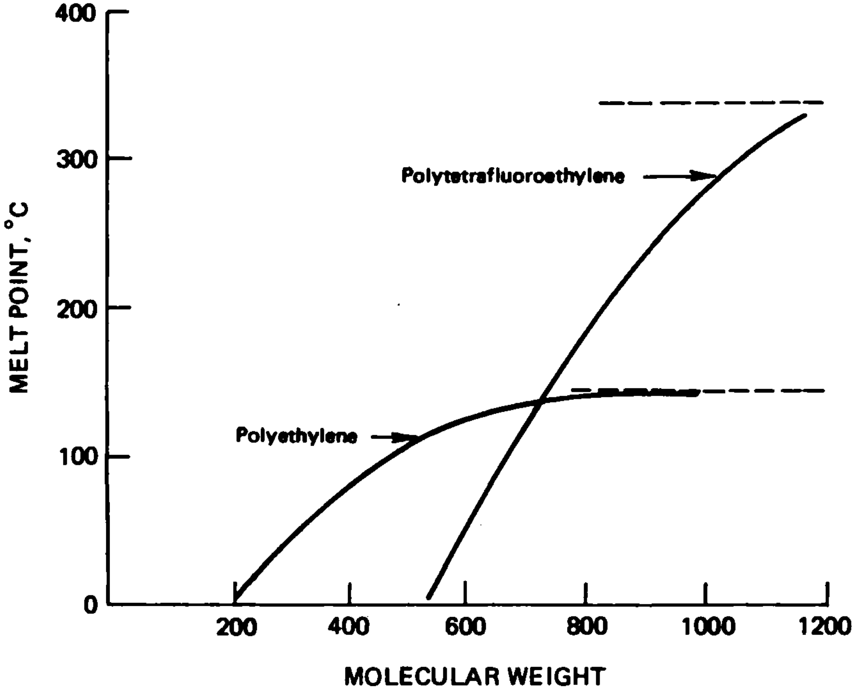
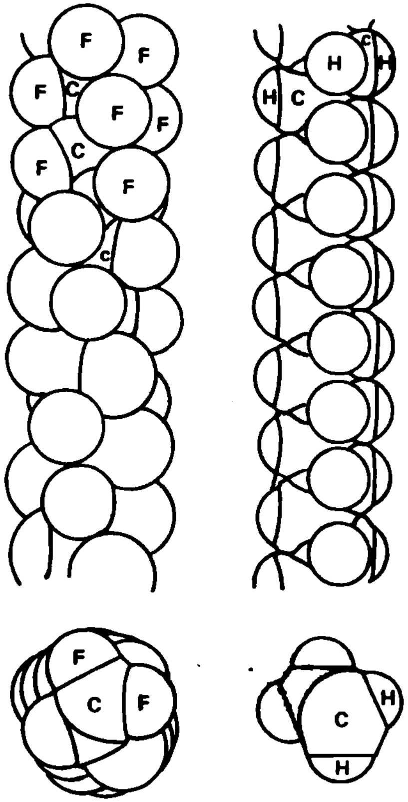


FIGURE 3 Melting point/molecular weight relationship.



Polytetrafluoroethylene
Side and End Views

Polyethylene
Side and End Views

Source: Taken from C. W. Bunn and E. R. Howells, *Nature* 174:549, 1954.

FIGURE 4 Chain structures in polytetrafluoroethylene and polyethylene.

Chemical Resistance and Frictional Properties

The bulky fluorine atom, in addition to as forcing the helical configuration characteristic of a PTFE molecule also forms an essentially continuous protective sheath around the carbon backbone, thus providing excellent protection from chemical attack, especially oxidative attack, on heat aging, an important functional parameter for a wire insulation. Resistance to chemical attack is also a desirable property for an electrical insulation frequently exposed to fuels and cleaning fluids in end use.

Another useful property inherent in PTFE, low coefficient of friction, also results from the highly electronegative fluorine sheath around the carbon backbone, which provides low surface energy. This has an eminently practical implication when the reduced force required to pull fluorocarbon-insulated wires and cables through trays or conduit is considered in relation to the force required by conventional insulating materials.

Mechanical Properties

Commercial, high-molecular-weight PTFE provides good room-temperature mechanical properties (such as a 95,000 psi flexural modulus) that are retained at a useful level even at 260°C (10,000 psi flexural modulus), as is depicted in Figure 5. Furthermore, at cryogenic temperatures, PTFE takes on a high-yield strength, becoming much like copper metal in mechanical properties (Figure 6).

Electrical Properties

An ideal dielectric will have the electrical properties of a vacuum, that is, a dielectric constant of 1 and a dissipation factor of 0. PTFE comes close to this ideal, the dielectric constant of a well-fabricated part being 2.07 and the dissipation factor, 0.00002 to 0.0004 over the range of 10^2 to 10^9 Hz (11). Its low-loss character is relatively independent of other variables, making it ideal for both power-and coaxial-cable insulation.

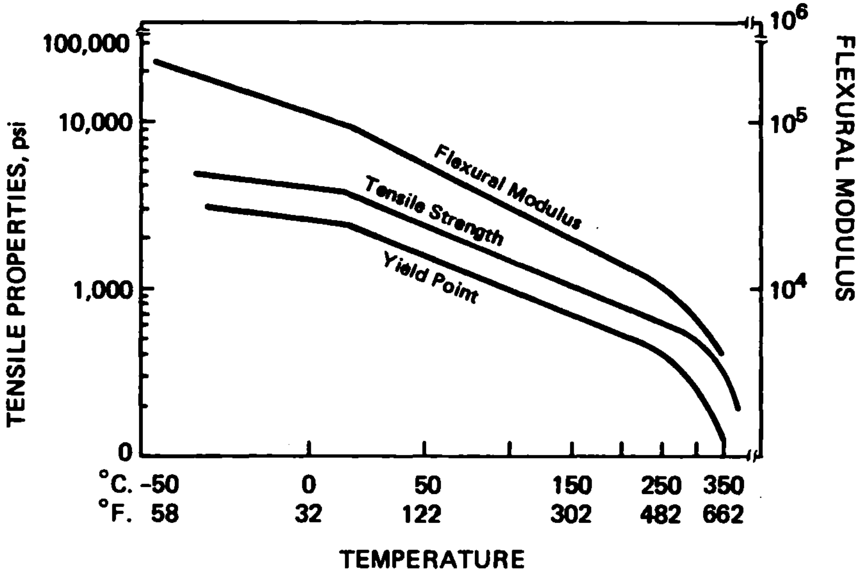


FIGURE 5 Tensile properties of Teflon as a function of temperature.

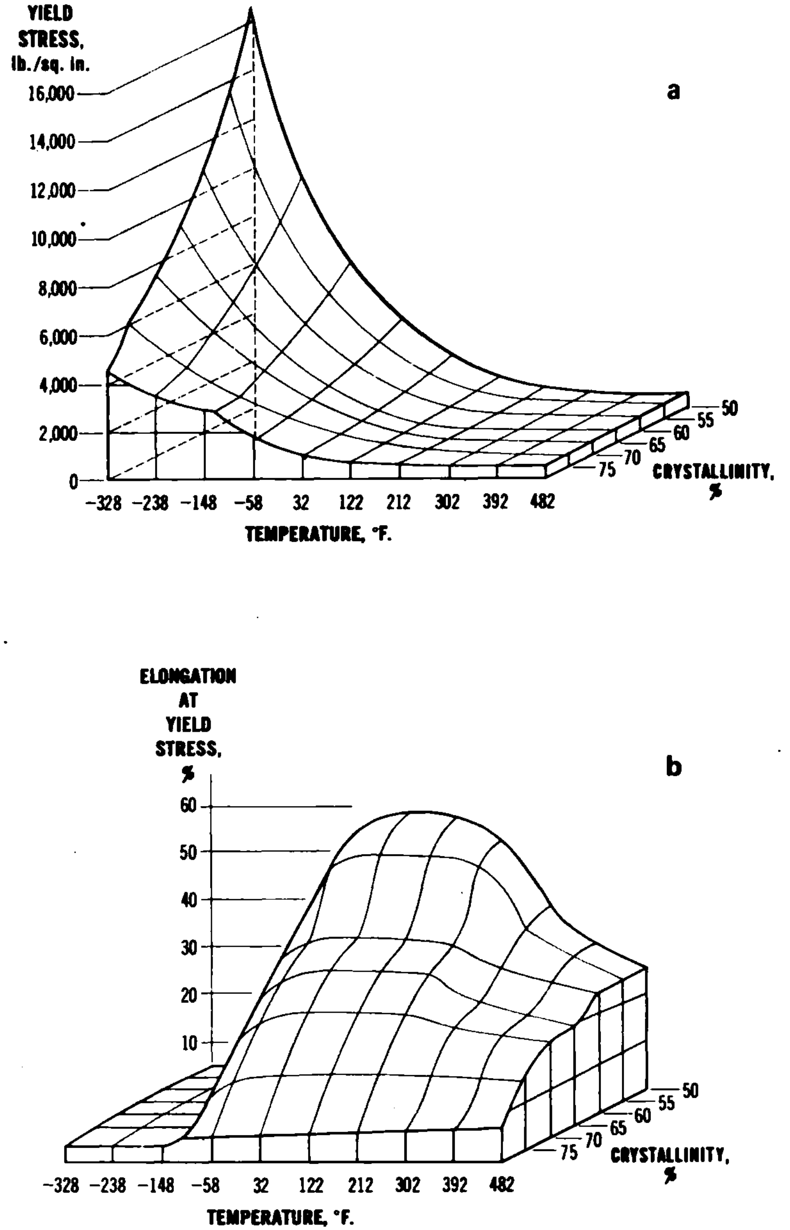


FIGURE 6 (a) Yield strength of Teflon TFE-fluorocarbon resins versus temperature at various crystallinity levels (ASTM D638-52T). (b) Elongation of Teflon TFE-fluorocarbon resins at yield stress versus temperature at various crystallinity levels (ASTM D638-52T).

These attractive electrical characteristics result from the balanced structure of the PTFE molecule, which, unlike many other common polymers, contains no dipoles (Figure 7).

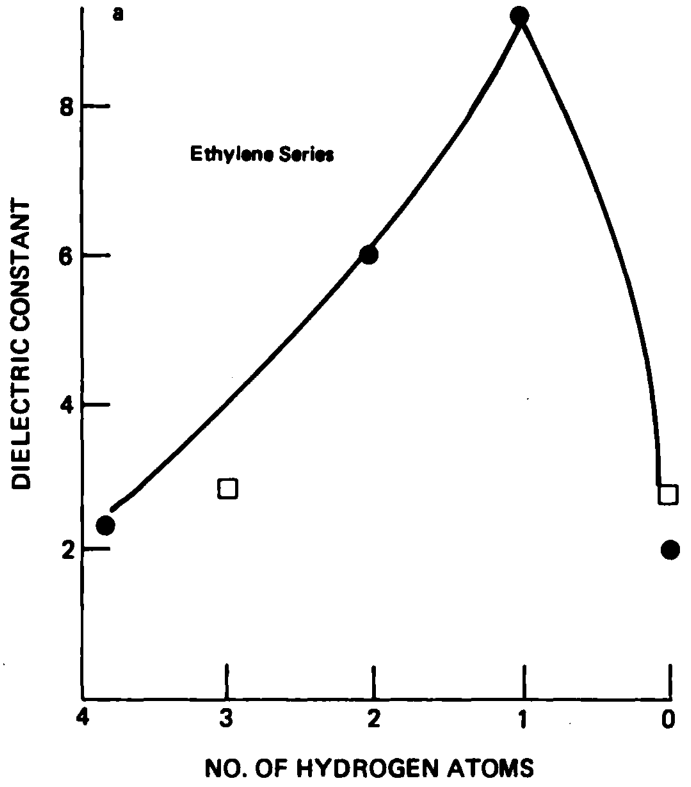
Weathering

Since PTFE is essentially transparent to solar UV wavelengths and contains no additives, it is unaffected by weathering, an important consideration for exposed insulations. It is interesting to note that glass cloth impregnated with PTFE is finding application in "space encapsulation," typified by the roof structure of the Pontiac stadium. It is eminently suitable for this end use because of its nonburning and soil-repellent character.

Thus, the configuration of the carbon and fluorine atoms in the molecular structure of the PTFE provides a unique combination of thermal, chemical, frictional, and electrical properties. One disadvantage from the processing point of view is the fact that PTFE is nonmelt processible. Indeed, as was mentioned previously, at its crystalline melting point, PTFE has the viscosity of lead at room temperature. This means that special processing techniques such as "paste extrusion" have to be used for conversion of PTFE "fine powder" homopolymer resin to electrical insulation.

Melt Processible Fluorocarbon Polymers

As was discussed earlier, simply lowering the molecular weight of PTFE to obtain a meltable polymer leads to a brittle product. Since this is partly due to the inherently excessive crystallization of the short molecular chain from the melt, research was undertaken to find an alternate way of preventing excessive crystallization. It was discovered that incorporation of a comonomer, hexafluoropropylene, permitted good properties to be maintained while lowering the viscosity of the original PTFE homopolymer by a factor of 1 million (measured at 380°C), and this provided the desired melt processibility. The fully fluorinated molecular structure essential for retention of the unique balance of properties desired for a high-performance dielectric material is, of course, retained.



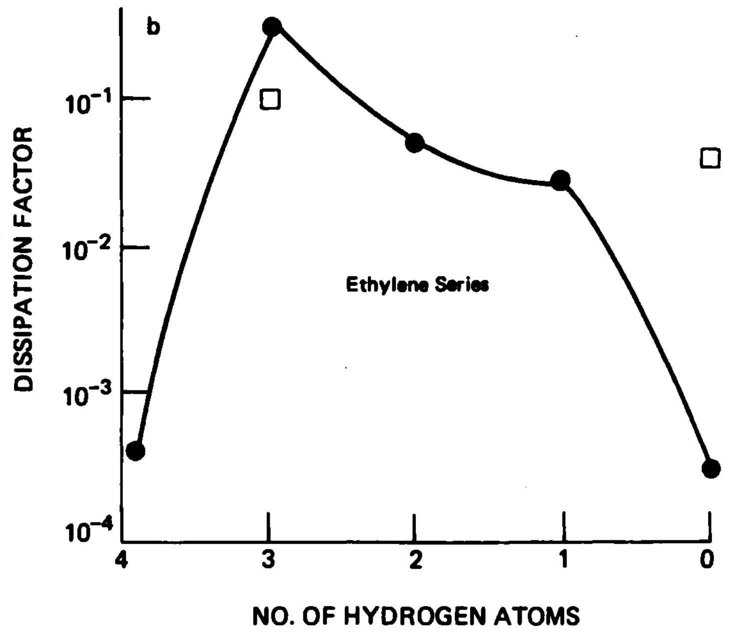


FIGURE 7 (a) PTFE dielectric constant. (b) PTFE dissipation factor.

Fluorinated Ethylene Propylene (Teflon FEP)

The first, fully fluorinated, melt-processible resin, Teflon FEP, was introduced in 1960. Introduction of the hexafluoropropylene unit leads to a slightly reduced upper-service temperature rating, along with a slight decrease in dielectric and frictional properties relative to the original PTFE property spectrum (Tables 1 and 2). The benefits of melt processibility can be realized in the manufacture of electronic components, such as coaxial spacers, by the relatively inexpensive injection molding process, while wire insulation in very long lengths becomes a reality. This copolymer is described fully in reference (3).

Ethylene/Tetrafluoroethylene (ETFE)

If one had to select an area for improvement in the broad spectrum of Teflon FEP properties, it would be in its mechanical toughness as thin wall insulation in mechanically abusive environments (such as those occurring in handling of huge harnesses in airframe- or transit-car wiring). Extensive research led to the development of a fluoropolymer having about a four- to fivefold improvement in cut-through resistance over Teflon FEP at equivalent thickness. This was achieved by the incorporation of ethylene, rather than hexafluoropropylene, into the homopolymer chain. This fluoropolymer (Tefzel), which is structurally modified to overcome the tendency of the simple copolymer to stress crack under the influence of temperature, is described more fully in reference (4).

Again, a modest trade-off in properties of this melt processible resin (Tables 1 and 2) had to be made in its upper use temperature, along with some changes in frictional and dielectric properties because the combination of hydrogen and fluorine makes the structure somewhat more polar. The doubling of flexural modulus and the improvement of impact strength and cut-through resistance were well worth this sacrifice, especially because a bonus of excellent radiation resistance was realized while good chemical resistance was retained.

The four- to fivefold improvement in cut-through resistance in thin wall insulation or jacketing of Tefzel is a highly desirable characteristic for wire insulation

TABLE 1 General Properties of Teflon and Tefzel

Property	Teflon TFE	Teflon FEP	Teflon PFA	Tefzel
Chemical resistance: hydrocarbons, ethylene glycol, battery acid, brake fluids, other chemicals	No effect	No effect	No effect	No effect
Resistance to weathering	No effect	No effect	No effect	No effect
Water absorption (ASTM D 570), %	<0.1	<0.1	<0.1	<0.1
Flammability (UL 83, vertical wire flame test)	No afterburn	No afterburn	No afterburn	No afterburn
Melting point, °F	621	530	590	520
Melting point, °C	327	275	300	270
Upper service temperature, °F				
1,500-2,000 hours estimated	550	450	550	400
20,000 hours	500	400	500	300
Cold bend @ -65°C, 2.5 kV for 5 min	Pass	Pass	Pass	Pass
Specific gravity	2.15	2.15	2.15	1.70

TABLE 2 Mechanical and Electrical Properties of Teflon and Tefzel

Property	Teflon TFE	Teflon FEP	Teflon PFA	Tefzel
Tensile strength, psi (73°F) ASTM D638	3,500	3,000	4,000	6,500
Elongation, % (73°F) ASTM D638	350	300	300	200
Flexural modulus, psi (73°F) ASTM D790	95,000	95,000	95,000	200,000
Flex life, MIT (7-9 mils) 180° flexes	750,000	100,000	200,000	30,000
Impact strength, ft-lb/in. ASTM D256				
Room temperature	No break	No break	No break	No break
- 65°F	30	10	10	>20
Coefficient of friction >10 fpm, 100 psi	0.1	0.3	0.2	0.4
Dynamic cut-through (lbs) Instron 1/16 in. radius blade moving at 0.2 in./min				
23°C	56[a] 129[b]	49[c] 118[d]	-	354[e]
75°C	43[a] 82[b]	25[c] 73[d]	-	132[e]
Dielectric constant, ASTM D50	2.1	2.1	2.1	2.6
Volume resistivity, ohm-cm ASTM D257	$>10^{18}$	$>10^{18}$	$>10^{18}$	$>10^{16}$
Dissipation factor, 10^3 Hz	<0.00001	0.00008	0.00001	0.0008

[a] 0.016-in. insulation thickness.

[b] 0.033-in. insulation thickness.

[c] 0.017-in. insulation thickness.

[d] 0.031-in. insulation thickness.

[e] 0.020-in. insulation thickness.

because for 600- and 1000-V-rated constructions, the wall thickness of insulation is not governed by electrical properties but by mechanical requirements. For example, 47 mils of cross-linked polyethylene (XLPE) is required to provide the cut-through equivalent of 20 mils of Tefzel for #12 AWG wire (Table 3). Interestingly enough, at the cut-through level exhibited by Tefzel, the load is likely to cut through the copper conductor.

The advantages of being able to use a tough thin wall insulation lie in space saving (6). For example, in a given 1-in.^{2} space one can fit 70 12-gauge wires with 20-mil wall insulation of Tefzel but only 35 of the same size wires insulated with the 47 mils of XLPE needed for equivalent cut-through strength (Figure 8).

Of course, with thin wall insulation there is less fuel value present in a fire situation.

Perfluoroalkoxy Resin (Teflon PFA)

An ultimate research goal was to achieve melt processibility with essentially no compromise in the unique combination of properties of PTFE homopolymer. This was achieved in 1976 with a copolymer containing a completely fluorinated backbone but with the necessary side groups connected by means of an oxygen link to provide greater flexibility at the branch point. This perfluoroalkoxy side group performs the same role as the trifluoromethyl pendant group in Teflon FEP, but with this copolymer there is only a very subtle trade-off in any properties. Specifically, dielectrics and upper, end-use temperature are remarkably close to those of PTFE (Tables 1 and 2), although there is an actual improvement in high-temperature mechanical properties (2.5-fold in flexural modulus, 2-fold in tensile creep at 250°C). A surprising observation has been the actual significant gain in tensile properties of tensile bars aged near the melting point. This product is finding application in chemically abusive environments as injection-molded wafer baskets used in the preparation of silicon semiconductors. Reference (5) contains a complete description of this new polymer.

In summary, melt processibility has been achieved with only minor deviation from the unique combination of properties of the original PTFE. Teflon FEP, the first copolymer, has an upper-use temperature of 200°C. Tefzel, a

TABLE 3 Dynamic Cut-Through #12 AWG Wire[a]

Insulation	Wall Thickness (mils)	Dynamic Cut-Through (lb) 23°C	75°C
Teflon TFE	16	56	43
Teflon FEP	17	49	25
Tefzel	20	380	115
Neoprene	77	80	45
Chlorosulfonated polyethylene	75	112	38
Cross-linked polyethylene	47	370	50
Cross-linked PVC	30	110	18

[a] UL test using 1/16-in. radius blade moving 0.2 in. per minute.

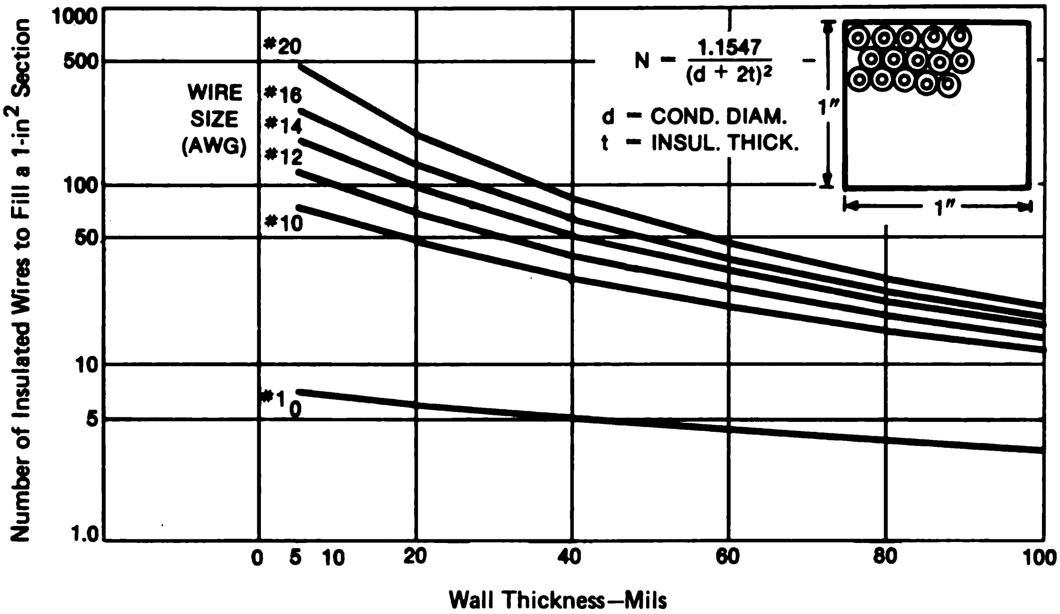


FIGURE 8 Space factor in multiconductor cables (effect of insulation thickness).

tough fluoropolymer, has been developed for severe mechanical applications at a conservative upper-use temperature of 150°C, and finally Teflon PFA is essentially a melt fabricable analog of the original PTFE polymer discovered by Plunkett 40 years ago.

POLYIMIDES

Structure

A logical starting point for a discussion of polymers based on carbon, hydrogen, and nitrogen is "66" nylon, a polyamide consisting of an aliphatic backbone with C-H and N-H bonds that are relatively weak and susceptible to oxidative attack on heat aging (Figure 9a). Other polyamides have been made with aromatic C-H linkages that are less susceptible to oxidative attack and have very good thermal stability (Figure 9b). This structure still contains a thermally unstable N-H link; however, this can be avoided if the nitrogen is attached directly to an aromatic ring rather than to the hydrogen. This structure (Figure 9c) is that of a polyimide (7). Aromatic polyimides exhibit extremely good thermal stability, but, unfortunately, a polymer based on this very rigid series of ring structures is practically impossible to fabricate into useful articles. When modified by introduction of a biphenyl ether link in between the imide units, this stiffness is moderated, and a flexible, tough, highly thermally stable polymer (Figure 9d) emerges.

Fabrication

Like most aromatic polyimides this polymer does <u>not</u> melt and hence cannot be melt fabricated by conventional techniques. It is made commercially by a series of chemical reactions that produce the film directly in a continuous process, and this material is well known as Kapton polyimide film.

The product is a thin, naturally amber-colored film that can be applied to wire in a tape-wrapping operation or laminated to copper for conversion to flexible printed circuits. The resultant thin, tape-wrapped, wire insulation is sealed to itself (or to the substrate) by a very thin film of Teflon FEP applied to the original polyimide film and may be topcoated with a liquid polyimide enamel or Teflon FEP.

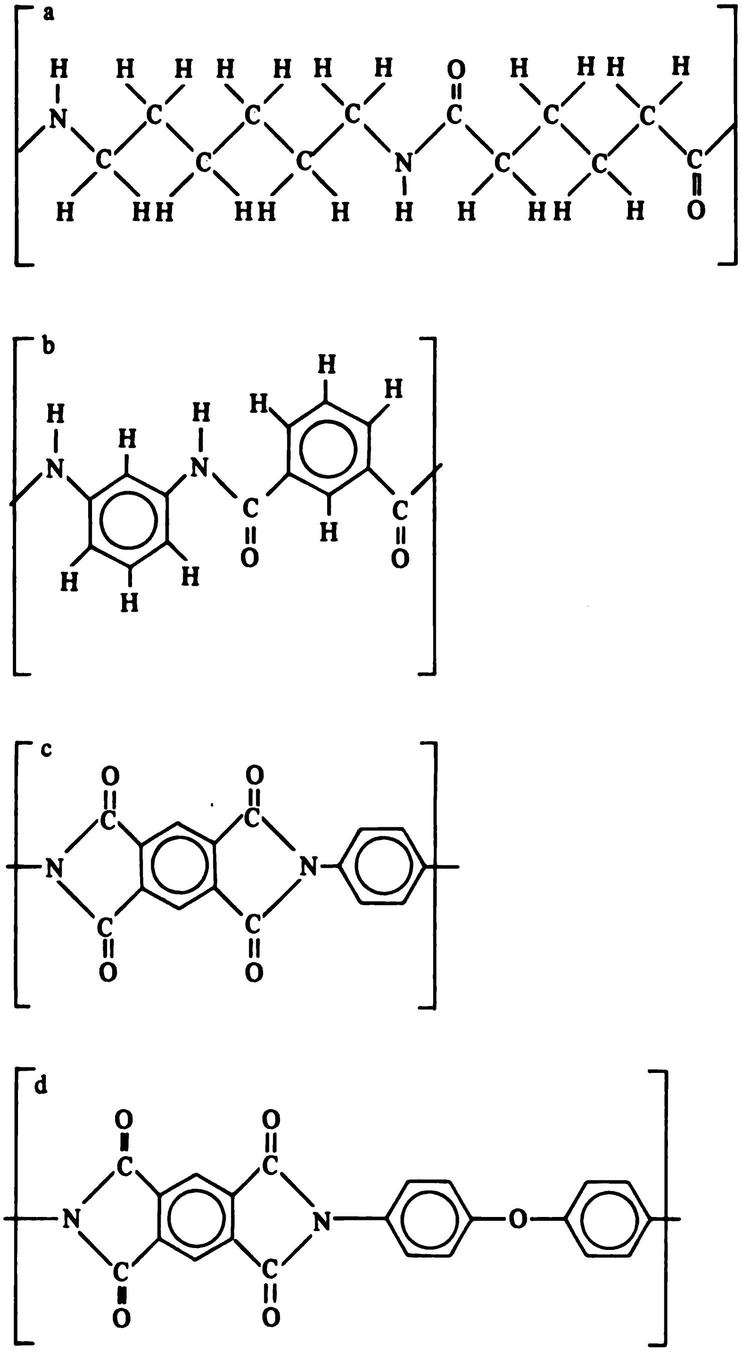


FIGURE 9 (a) Nylon "66," a polyamide. (b) A high-temperature polyamide. (c) A polyimide. (d) Kapton polyimide.

Properties

In film form the flexible polyimide has some interesting mechanical and thermal qualities (Tables 4 and 5). It simply does not melt and has enormous cut-through resistance at high temperature plus excellent flexibility for such a lightweight material. The useful temperature range is from -269°C to about 250°C continuously or to 400°C for short time periods. Kapton is generally resistant to a wide range of chemicals, the only limitation being a susceptibility to hydrolysis by strong aqueous bases. As far as radiation resistance is concerned, aromatic polyimides are outstanding. Kapton film has remained flexible to a 180° bend after 4,000 Mrads exposure to gamma irradiation. Dielectrically and mechanically, it is an excellent material. It is not quite as good as the fluorocarbons perhaps in some electrical properties, but it is unsurpassed in cut-through resistance per unit thickness. It is this dielectric/cut-through combination that makes Kapton such a good insulation for very thin wall miniature cables and flexible circuitry and enables it to survive the electromechanical abuse experienced, for example, in armatures of locomotive traction motors.

ELECTRICAL INSULATION IN A FIRE SITUATION

It is important to understand the response of an electrical insulation in a fire situation in terms of its generation of smoke particulates, as a source of fuel, as a flame propagator, and as a potential source of corrosive off-gases liberated if the insulation participates in the fire.

Smoke Generation

Although the relevance of laboratory smoke tests is still subject to some debate, the National Bureau of Standards Smoke Chamber method (National Fire Protection Association 258-T) has been widely used for comparison of polymeric materials under a particular set of conditions. Smoke - density data generated from wire samples wrapped on a sample holder under smoldering and flaming conditions have been reported in terms of time to achieve a maximum smoke density (Dm), and the time to achieve an optical smoke density of 16 (T16). Fully fluorinated polymers generate little or no smoke particulates in relation to conventional dielectrics, while hydrogen-containing fluoropolymers generate some smoke

TABLE 4 Polyimide (Kapton) 1-mil Film

PROPERTY	TYPICAL VALUES—1 mil film			TEST CONDITION	TEST METHOD
	% Tensile Retained	% Elongation Retained	% Modulus Retained		
CHEMICAL PROPERTIES				Days Immersed at Room Tempertaure	
CHEMICAL RESISTANCE TO.					
Benzene	100	82	100	365	
Toluene	94	66	97	365	
Methanol	100	73	140	365	
Acetone	67	62	160	365	
10% Sodium Hydroxide		Degrades		5	
Glacial Acetic Acid	85	62	102	36 days at 110°C	
p-Cresol	100	77	102	22 days at 200°C	
"Arochlor" **	100	53	142	365 days at 200°C	
Transformer Oil	100	100	100	180 days at 150°C	
Water pH — 1	65	30	100	14 days at 100°C	
pH — 4.2	65	30	100	14 days at 100°C	
pH — 7.0	65	30	100	70 days at 100°C	
pH — 8.9	65	20	100	14 days at 100°C	
pH — 10.0	60	10	100	4 days at 100°C	
RADIATION RESISTANCE					
Gamma (Savannah River)	Still Flexible (180° Bend)			Exposure 4.16 x 10[illegible] RADS	
Electron (Van de Graaff)	Retains 50% of Original Elongation			Exposure 6 x 10[illegible] RADS	
Neutron plus Gamma (Brookhaven)	Darkened but tough			Exposure 10[illegible] RADS	
UV	Excellent				Westinghouse Fluorescent Sunlamps Ozone Present, Dry Environment
FUNGUS RESISTANCE	Inert			12 months	Soil Burial
MOISTURE ABSORPTION	1.3% 2.9%			50% Relative Humidity at 23.5°C Immersion for 24 hrs. at 23.5°C	Constant Environment Room ASTM D-570-63
HYGROSCOPIC COEFFICIENT OF EXPANSION	2.2×10^{-5} in/in/% Relative Humidity			72°F 20% - 80% Relative Humidity	
PERMEABILITY					
Gas	cc/(100 in²) (24 hrs.) (atm/mil)			23°C	ASTM D-1434-63
Carbon Dioxide	45				
Hydrogen	250				
Nitrogen	6				
Oxygen	25				
Helium	415				
Water Vapor	gm/(100 in²) (24 hrs.)/mil 5.4				ASTM E-96-63T

CHEMICAL

PROPERTY	TYPICAL VALUES—1 mil film			TEST CONDITION	TEST METHOD
	−195°C	25°C	200°C		
ELECTRICAL PROPERTIES					
Short Term Dielectric Strength (1 mil)	10,800	7,000 volts	5,600 volts	60 cycles	ASTM D-149-64
Dielectric Constant		3.5	3.0	1 kilocycle	ASTM D-150-64T
Dissipation Factor		.003	.002	1 kilocycle	ASTM D-150-64T
Volume Resistivity		10[illegible] ohm cm	10[illegible] ohm cm		ASTM D-257-61
Surface Resistivity		10[illegible] ohms		50% Relative Humidity	ASTM D-257-61
Corona Start Voltage (1 mil)		465 volts		50% Relative Humidity	ASTM D-1868-61T
Insulation Resistance		100,000 megohm mfds			Based on 0.05 mfd. wound capacitor using 1-mil H Film

ELECTRICAL

Monsanto registered trademark

TABLE 5 Polyimide (Kapton) 1-mil Film

	PROPERTY		TYPICAL VALUES—1 mil film			TEST METHOD
			−195°C	25°C	200°C	
PHYSICAL	**PHYSICAL PROPERTIES**					
	Ultimate Tensile Strength	(MD)	35,000 psi	25,000 psi	17,000 psi	ASTM D 882-64T
	Yield Point	(MD)		10,000 psi at 3%	6,000 psi at 3%	ASTM D 882-64T
	Stress to Produce 5% Elongation	(MD)		13,000 psi	8,500 psi	ASTM D 882-64T
	Ultimate Elongation	(MD)	2%	70%	90%	ASTM D 882-64T
	Tensile Modulus	(MD)	510,000 psi	430,000 psi	260,000 psi	ASTM D 882-64T
	Impact Strength			6 Kg cm/mil		Du Pont Pneumatic Impact Test
	Folding Endurance (MIT)			10,000 cycles		ASTM D-2176-63T
	Tear Strength—Propagating (Elmendorf)			8 gm/mil		ASTM D-1922-61T
	Tear Strength—Initial (Graves)			510 gm/mil		ASTM D-1004-61
	Tear Strength—Initial (Graves)			1100 lb./in.		ASTM D-1004-61
	Bursting Test (Mullen)			75 psi		ASTM D-774-63T
	Density			1.42 gm/cc		ASTM D-1505-63T
	Coefficient of Friction Kinetic (Film-to-Film)			.42		ASTM D-1894-63
	Refractive Index (Becke Line)			1.78		Encyclopaedic Dictionary of Physics, Volume I
	Area Factor			136 ft^2/lb/mil		Calculation

	PROPERTY	TYPICAL VALUES—1 mil film				TEST CONDITION	TEST METHOD
THERMAL	**THERMAL PROPERTIES**						
	Melting Point	NONE					
	Zero Strength Temperature	815°C				20 psi load for 5 seconds	Hot Bar (Du Pont Test)
	Cut-through Temperature	435°C 525°C				1 mil 2.5 mil	Weighted Probe on Heated Film (Du Pont Test)
	Coefficient of Thermal Expansion	2.0×10^{-5} in/in/°C				(—) 14°C to 38°C	ASTM D-696-44
	Coefficient of Thermal Conductivity	3.72×10^{-4} $\frac{(cal)(cm)}{(cm^2)(sec)(°C)}$ 3.89×10^{-4} " 4.26×10^{-4} " 4.51×10^{-4} "				25°C 75°C 200°C 300°C	Model TC-1000 Twin Heatmeter Comparative Tester
	Flammability	Self-extinguishing when flame removed					
	Heat Sealable	No					
	Specific Heat	0.261 cal./gm./°C				40°C	Differential Calorimetry
		250°C	275°C	300°C	400°C		
	Shrinkage	0.3%		0.5%	3.0%	30 minutes	ASTM D-1204
	Heat Aging (in air)	8 yrs	1 yr.	3 months	12 hours	Circulating Air Oven	Time to Reach 1% Elongation

(Table 6). Polyimide insulation on wire also develops little smoke either under flaming or current overload conditions. The importance of smoke to human safety in a fire situation is not a disputed matter.

Flammability (Small-Scale Testing)

Various laboratory tests of flammability have been proposed over the years by both military and civilian standards groups for qualification of plastic materials for use as wire insulation. For instance, Underwriters Laboratories has sanctioned several burning tests, and many materials have been rated under test UL 83 and, more recently, UL 94, in which fluoropolymers rate 94 V-0, the most favorable category.

The "oxygen index" rating is now widely used as a laboratory measure of flammability (ASTM D2863). This puts both polyimides and the Teflon fluorocarbon resins in the range of exceptionally flame-resistant materials. The value for Tefzel is lower but still at an advantageous level (Table 7).

Although these tests can be extremely useful tools for initial studies on candidate materials or to screen flame-retardant additives, they do not necessarily predict a material's response to a real fire situation. We have felt the need for larger-scale testing of insulated cables to evaluate the total contribution (smoke, fuel, and propagation) of insulating materials, and we have joined with other concerned parties involved in the design of nuclear power facilities to run several large-scale flammability tests.

Flammability (Large-Scale Testing)

IEEE 383

As a starting point, the IEEE 383 test procedure was used to generate flame propagation data and to determine the effect of corrosive off-gases. The test configuration is shown schematically in Figure 10, where the flame impinges tangentially on insulated cables strapped in a vertical 8-ft cable tray.

TABLE 6 NBS Smoke Chamber #20 AWG Wire Samples (NFPA #258)

Insulation	Test Condition	D_m	Time to D_m (min)	Time to $D_m = 16$ (min)
Teflon TFE	F[a]	1	20	>20
	S[b]	0	20	>20
Teflon FEP	F	11	20	>20
	S	0	20	>20
Tefzel	F	290	20	2.3
	S	18	20	>20
Cross-linked polyethylene	F	150		
	S	350		
PVC	F	340	7	0.5
	S	210	20	5.0
Silicone rubber	F	337	20	2.6
	S	40	20	7.6
Ethylene/propylene rubber	F	450	6.5	1.0
	S	390	20.0	4.3

[a] F = Flaming test (radiant heat plus gas flame).

[b] S = Smoldering test (radiant heat only).

TABLE 7 Oxygen Index ASTM D2863

Insulation	OI
Teflon TFE	>95
Teflon FEP	>95
Teflon PFA	>95
Tefzel	30
XLPE-FR	30

Tefzel and a representative cross-linked flame-retardant polyethylene (XLPE-FR), both of which have an oxygen index of about 30, were evaluated as insulation and jacketing on a set of six cables made up of seven 14-gauge conductors by exposing them to a series of controlled flames. The cables made up of wire with 10 mils of insulation and 25 mils of jacketing of Tefzel exposed to a 400,000-Btu/hour flame burned in the flaming zone, with the fire consuming the available "fuel." Some smoke was observed, as was predicted by the NBS Smoke Chamber tests. When the flame was shut off after 20 min, the conductor glowed red hot, and the extent of the fire propagation was measured as about 6 ft of insulation destroyed; no propagation occurred beyond this point.

In the same burning environment, XLPE-FR burned with rapid fire propagation and flame spread, the production of copious smoke, and complete destruction of the entire 8 ft of the 20 mil insulated and 60-mil jacketed cables. This test is described more completely in reference (9).

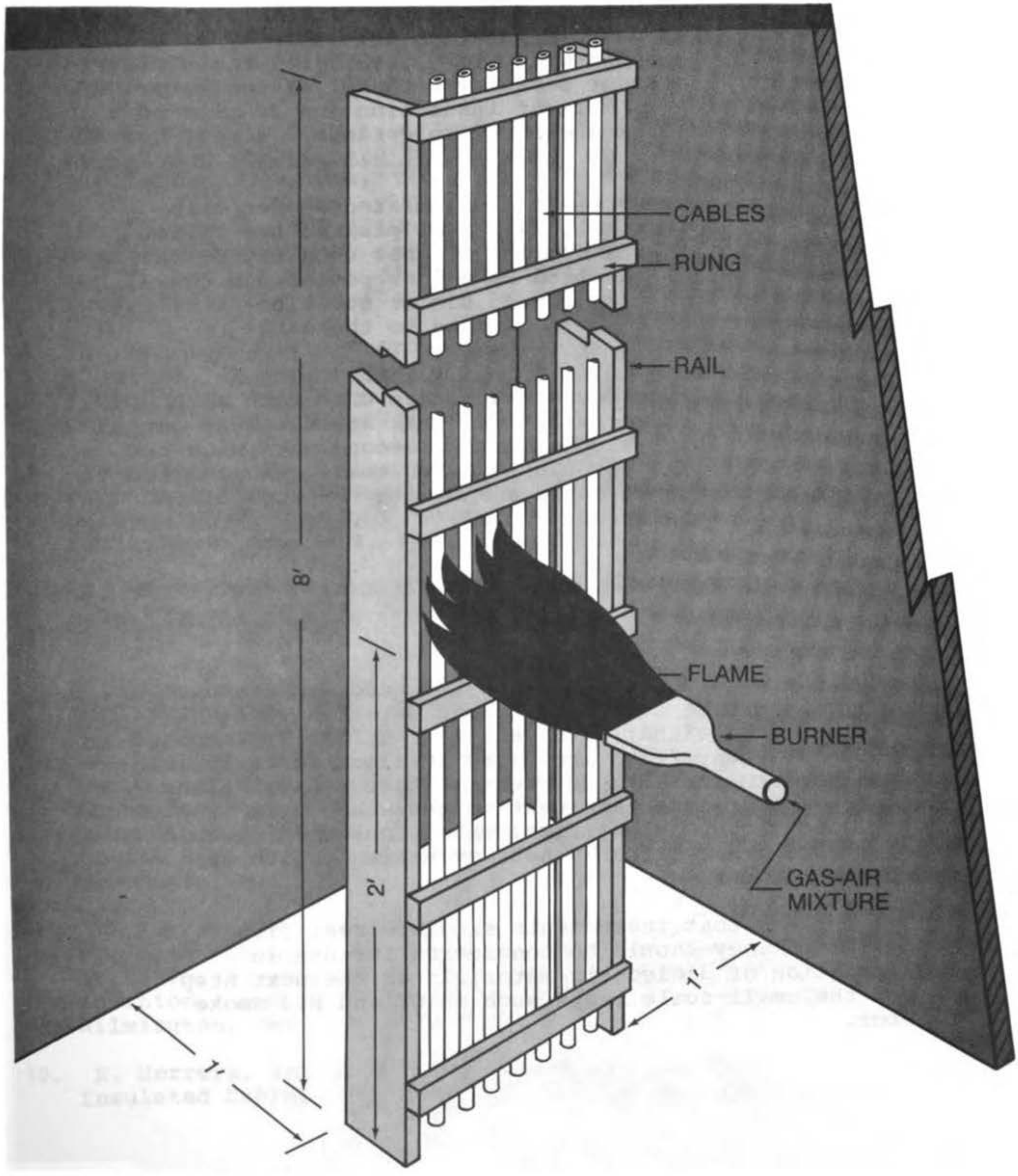
During these tests we had the opportunity to measure the extent of corrosion of copper tags (located on the vertical cable rack shown in Figure 10) induced by the off-gases from the burning insulation. The XLPE-FR off-gas had a fourfold greater corrosive effect on the copper tag than that evolved from Tefzel.

Steiner Tunnel

Following the example of Bell Laboratories (8), the ASTM E-84 test, modified to carry cables, was also run on Tefzel and XLPE-FR. This is the so-called 25-ft Steiner Tunnel Test. In this test, the eight cables insulated and jacketed with Tefzel provided a flame spread of 3-1/2 ft beyond the burner flame, destroying 8 ft of cable insulation after 20-min (rather than the usual 10-min) exposure to the 4-1/2-ft, 300,000-Btu/hour igniter flame and controlled, 240 ft/min airflow.

In contrast, flame spread with XLPE-FR insulated cables was 17-1/2, ft and the cable was completely destroyed.

Figure 10. IEEE Schematic Arrangement for Flame Testing



Open and Closed Cable Trays (Trash Fire)

Flame tests have also been run at the Southwest Research Institute (SWRI) to evaluate fire propagation resulting from the use of Tefzel as cable insulation initiated by a simulated trash fire. In these tests, vertical cable trays were filled to 40 percent capacity with 202, 7-conductor, #14 AWG cables with 10 mils of insulation and 20 mils of a jacket of Tefzel (10) and exposed to "standard fires" based on wooden cribs.

The first fire source was a calibrated wooden crib simulating a fire started in a 32-gal plastic bag filled with disposable clothing typical of that used in nuclear installations. This supplied a heat output of 300,000 Btu/hour to the open tray for 15 min or so. The fire resulted in some smoke but no damage to the cable insulation.

A more severe fire source--a wooden crib with more prolonged burning characteristics (peak average heat output of 500,000 Btu/hour)--was used for a second test with the open cable tray. The fire burned with some smoke and led to about 4 ft of destroyed cable again with no propagation along the cable insulation.

Circuit Integrity

Although there is no consensus on the need for circuit integrity in a fire situation, tests were run using 12 cables insulated either with Tefzel or Teflon FEP exposed to a 210,000-Btu/hour flame intensity in a configuration close to that used in the IEEE 383 test. These constructions included a mica-wound tape next to the conductors as a thermal and mechanical barrier, which conferred circuit integrity of greater than 1 hour even with deliberate mechanical abuse.

We believe that these tests simulate real fire conditions. They should be considered for use in qualification of dielectric materials as the next step beyond the small-scale tests such as OI and NBS Smoke Chamber.

REFERENCES

1. J. O. Punderson. Fluorocarbon resins from the original polytetrafluoroethylene (PTFE) to the latest melt processible Copolymerc. Technical papers presented at Society of Plastics Engineers, Mid-Ohio Valley Bicentennial Regional Technical Conference No. 30, December 1, 1976.

2. D. I. McCane. Polytetrafluoroethylene. In *Encyclopedia of Polymer Science and Technology*, vol. 13, Interscience Publishers, New York, 1970, pp. 623-654.

3. D. I. McCane. Tetrafluoroethylene copolymers with hexafluoropropylene. In *Encyclopedia of Polymer Science and Technology*, vol. 13, Interscience Publishers, New York, 1970, pp. 654-670.

4. L. Johnson. Tetrafluoroethylene copolymers with ethylene. *Encyclopedia of Polymer Science and Technology*, suppl. vol. 1, Interscience Publishers, New York, 1976, pp. 260-278.

5. L. Johnson. Tetrafluoroethylene copolymers with perfluoroalkoxy pendant groups. *Encyclopedia of Polymer Science and Technology*, suppl. vol. 1, Interscience Publishers, New York, 1976, pp. 260-267.

6. J. R. Perkins. New materials techniques reduce cable bulk. *Electr. World*, October 1, 1975.

7. C. E. Sroog. Polyimides. In *Encyclopedia of Polymer Science and Technology*, vol. 11, Interscience Publishers, New York, 1969, pp. 247-272.

8. J. R. Beyreis, J. W. Skjordahl, S. Kaufman, and M. M. Yocum. A Test Method for Measuring and Classifying the Flame Spreading and Smoke Generating Characteristics of Communications Cable. Paper presented at Twenty-Fifth Annual Wire and Cable Symposium, Cherry Hill, N. J., November 16-18, 1976.

9. J. R. Perkins, and J. Ryan, Sr. Fire Tests--Insulated Wire and Cable. Report on tests conducted September 27-29, 1976, by General Electric Nuclear Systems Division, location, and E. I. DuPont de Nemours and Company, Wilmington, Del., January 1977.

10. R. Herrera, and J. Beitel. Fire Tests on Tefzel Insulated Cables. Final Report, Project No. 03-4685-115,

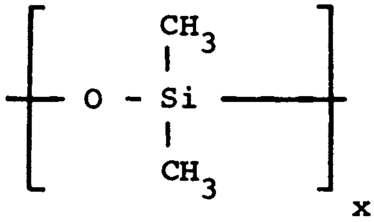
Southwest Research Institute, San Antonio, Texas, March 1977.

11. Electronic Electrical Design Data for Teflon. Booklet A66426, E. I. DuPont de Nemours and Company, Wilmington, Del.

COMBUSTION, FLAMMABILITY, AND FIRE HAZARD PROPERTIES OF SILICONES

Jonathan Lipowitz
Dow Corning Corporation, Midland, Michigan

This paper reviews the combustion, flammability, and fire hazard properties of polydimethylsiloxane rubber wire and cable materials. The chemistry of the combustion process for polydimethylsiloxane fluids has been studied in detail(1, 2) and will be reviewed first with particular emphasis on the products of combustion. Because the structure of the rubber materials is closely related to that of the high molecular weight fluids, details of the combustion process and the combustion products will be similar. The structure of the polydimethylsiloxanes is shown below:



$$\left[-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}- \right]_x$$

The degree of polymerization (X) of the fluids studied ranged up to 100. The degree of polymerization of the gums used in silicone rubber formulations range from 3,000 to 5,000. Keep in mind that the silicone fluids are appreciably more volatile than are the silicone rubbers, especially after the latter have undergone crosslinking, and thus the fluids are considerably more combustible.

Typical silicone rubber wire and cable formulations are as follows:

Typical Dimethyl Silicone Wire/Cable Formulation

- 100 parts $(Me_2SiO)_x$ gum
  (~0.1 part CH_2=CHMeSiO)
- 50-80 parts SiO_2 (fumed silica)
- 1.5 parts peroxide
- Several parts additives

Typical Phenyl Methyl Silicone Wire/Cable Formulation
(Good Low-Temperature Properties)

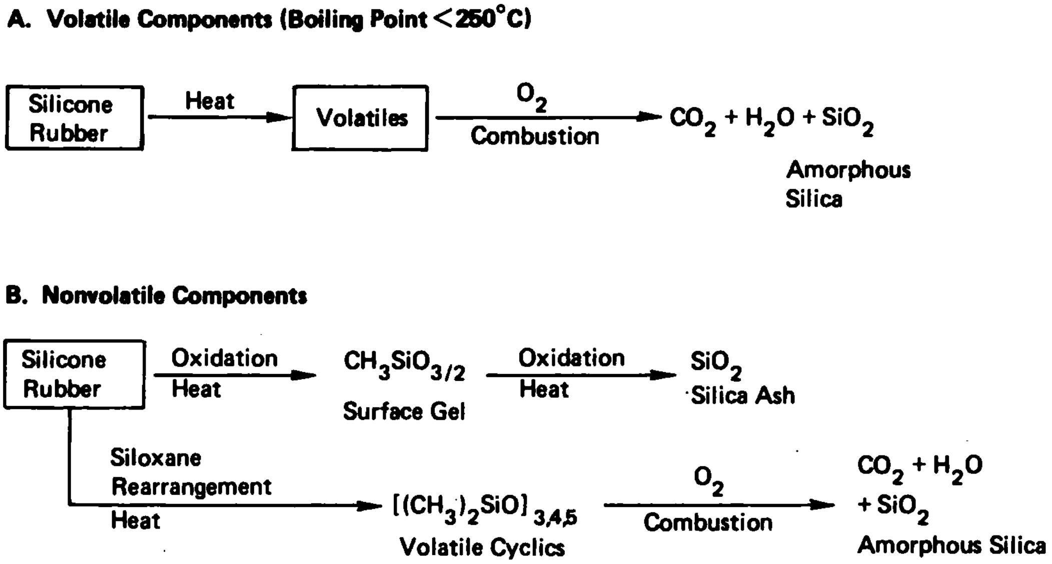
- 100 parts $(Me_2SiO)_x$
- (4 parts C_6H_5MeSiO + 0.1 part CH_2=CHMeSiO)
- 50-80 parts SiO_2 (fumed silica)
- 1.5 parts peroxide
- Several parts additives

A dimethyl rubber contains 100 parts of polydimethylsiloxane gum and about 0.1 percent of vinylmethylsiloxane functionality incorporated into the gum to aid in crosslinking; 50-80 parts of a high-surface-area, fumed silica; 1.5 parts of peroxide for crosslinking; and several parts of various other components, including pigments and thermal- and oxidative-stability additives. A phenylmethyl rubber formulation incorporates some phenylmethylsiloxane to improve low-temperature properties. It contains 100 parts dimethylsiloxane gum with 4-5 percent phenylmethylsiloxane and 0.1 percent vinylmethylsiloxane and several parts of additives, including pigments and stability additives. Good reviews of silicone rubber technology are available (3).

COMBUSTION OF POLYDIMETHYLSILOXANES

Figure 1 is a scheme for the combustion of high-molecular-weight, low-volatility silicones, including the silicone rubbers. Volatile components are present in very small amounts in a silicone rubber. These components will volatilize on heating and undergo combustion in the gas phase, as is shown in path A.

Nonvolatile material undergoes combustion by two simultaneous processes (path B). Surface oxidation occurs to some extent, giving a monomethylsiloxane surface gel intitially, which upon further exposure is oxidized to a silica ash. Along with surface oxidation, the well-known siloxane rearrangement reactions occur to give volatile cyclic siloxanes of degrees of polymerization 3, 4, 5, and



A. Volatile Components (Boiling Point <250°C)

B. Nonvolatile Components

FIGURE 1 Volatile evolution during burning.

higher. These volatile cyclics then undergo combustion in the gas phase. Siloxane rearrangement is a catalyzed process that becomes rapid above 350°C. Therefore, volatile evolution from silicone rubbers becomes appreciable only above 350°C.

Figure 2 shows a burning polydimethylsiloxane fluid of a degree of polymerization of approximately 50. The silica ash is clearly visible. This white reflective ash layer serves to protect material beneath from the radiant energy of the flame. Gas-phase, or flaming combustion of volatile cyclic siloxanes is clearly visible and primarily occurs at gaps and cracks in the silica layer. Some areas of glowing silica are visible. Solid-phase combustion appears to occur at these regions of glowing silica, with fuel supplied through the silica layer by a wicking mechanism. The typical white or light gray smoke of silicone flames is seen, which is composed almost entirely of amorphous silica. Much visible light is emitted from the luminous, yellow white flames by the small silica particles present, causing these flames to appear hotter than is indicated by actual flame temperatures, which are comparable to those of aromatic organics.

Figure 3 shows the appearance of a typical organic polymer and a silicone rubber after burning. Both materials have a Limiting Oxygen Index of 25. The black carbonaceous char of the organic material can be contrasted with the white, voluminous silica ash produced on burning the silicone rubber.

Figure 4 shows a model for combustion of low-volatility polydimethylsiloxanes, including the silicone rubbers. On heating a nonvolatile polydimethylsiloxane polymer above 350°C, volatile cyclic dimethylsiloxanes are evolved by the siloxane rearrangement process. The cyclics undergo combustion in the gas phase. Energy feedback from the flame serves to pyrolyze more cyclics and thus to continue the burning process. Simultaneously, surface oxidation is occuring to produce a totally oxidized silica ash on the surface and a partially oxidized monomethylsiloxane gel layer beneath. The reflective ash and gel layers serve to shield the polymer lying beneath from energy feedback from the flame. The combustion products in this process, an excess of oxygen being assumed, are carbon dioxide, water, and amorphous silica.

FIGURE 2. Polydimethylsiloxane Fluid 50 cs, Burning in Air

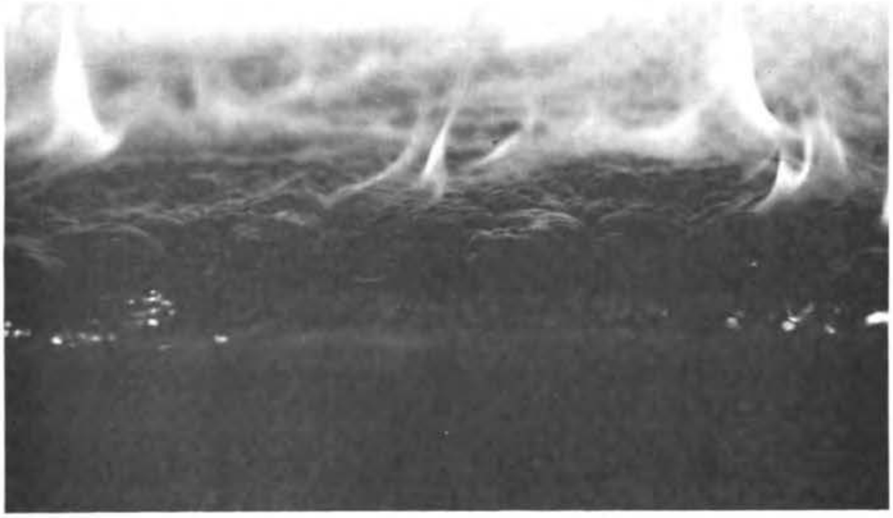
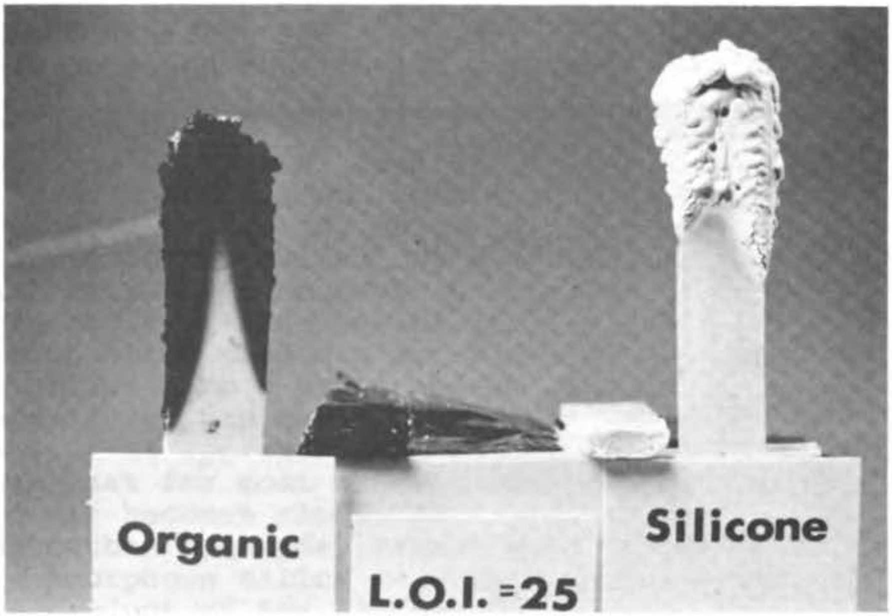


FIGURE 3. Organic Polymer and Silicone Rubber After Burning



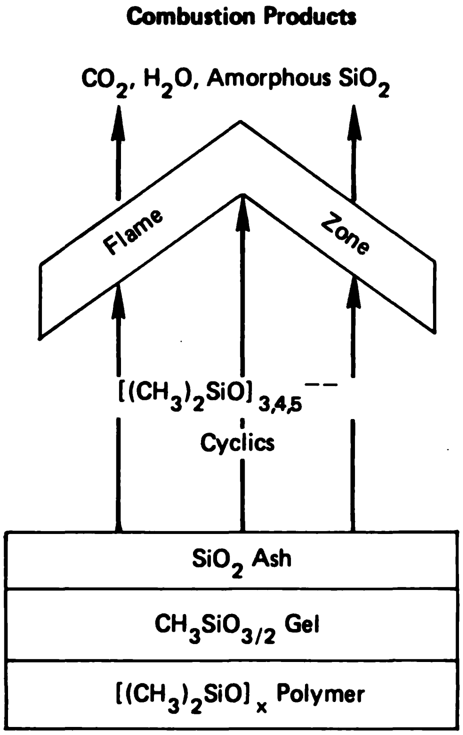
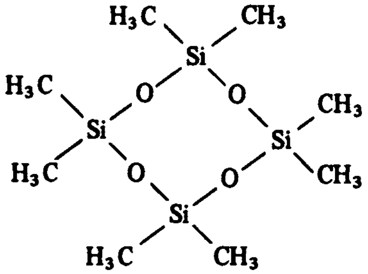


FIGURE 4 Model for burning of low-volatility polydimethylsiloxanes.

Let us look at the combustion process in more detail. Octamethylcyclotetrasiloxane, or D_4, is a major volatile fuel produced on siloxane rearrangement and was therefore chosen for detailed study. D_4 is a fluid of boiling point 175°C.



Calculations of adiabatic combustion products and flame temperature were made for D_4 using a computer program provided by Dr. Stull of the Dow Chemical Company. Combustion was calculated in air at 1 atm with D_4 initially in the liquid state at 25°. The calculation method is based on stoichiometry and equilibrium constants (4).

Figure 5 shows the results of calculations for D_4 combustion over a range of fuel to air ratios. Moles of product per mole of fuel and adiabatic flame temperature (T) are plotted against Φ, which is the ratio of fuel to stoichiometric fuel required for complete combustion. The fuel-to-air ratio is also shown as a volume percent of fuel in air. In the fuel-lean region ($\Phi < 1$), with an excess of air, the combustion products are water, carbon dioxide, and amorphous silica with a small amount of nitrous oxide. Flame temperatures are maximum near the stoichiometric region ($\Phi = 1$) at approximately 2100°C, which is slightly higher than that for most organic materials. As a mixture of fuel to air becomes richer ($\Phi > 1$), hydrogen, rather than water, and carbon monoxide, rather than carbon dioxide, are produced. Amorphous silica remains almost the exclusive combustion product of the silicon originally present in the fuel. At the stoichiometric point for this reaction (Φ =

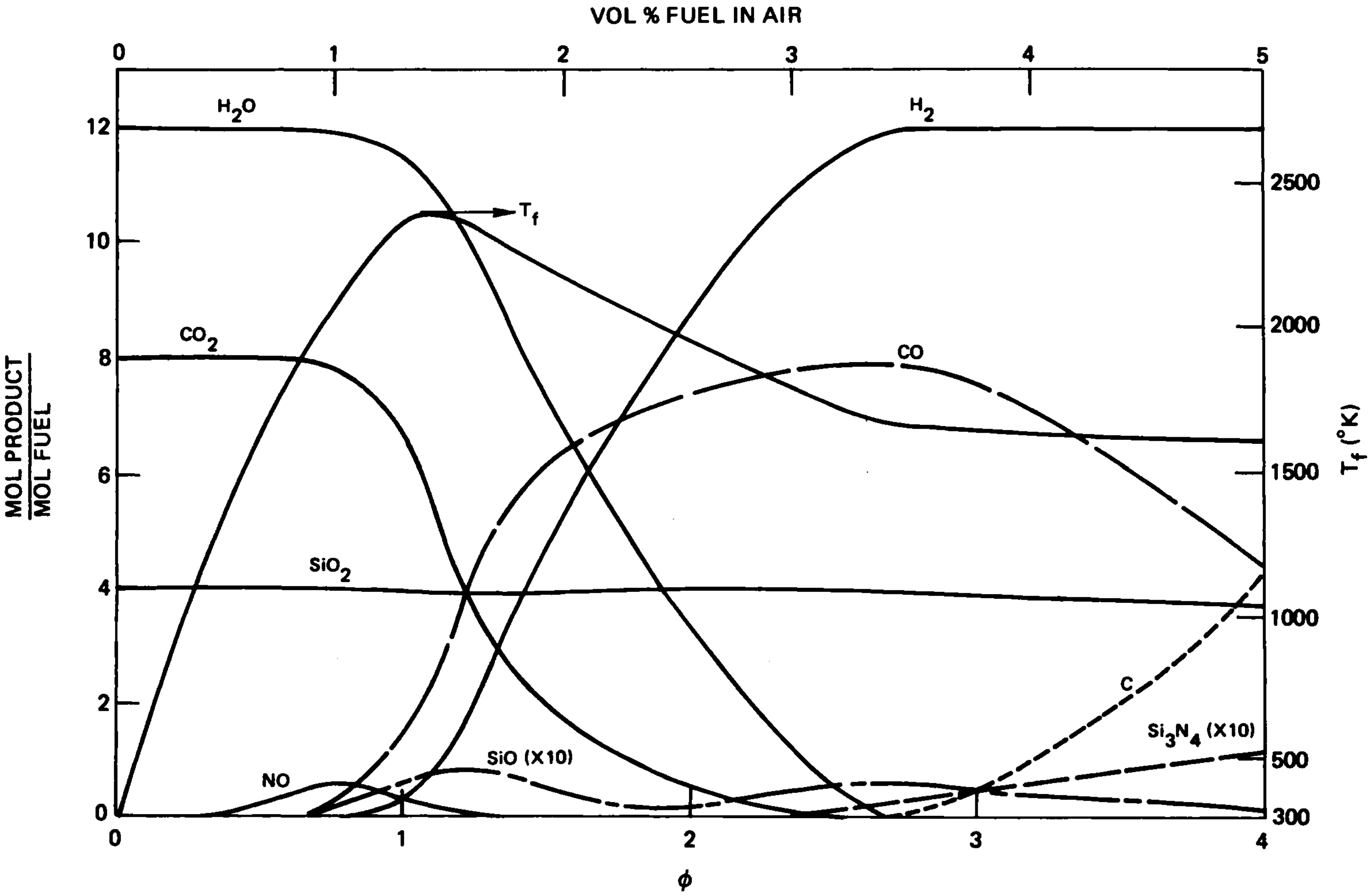


FIGURE 5 Calculated adiabatic combustion products and flame temperature for $[Me_2SiO]_4$ (ℓ) (298°K in air, $\Delta H_f^\circ = -518$ kcal/mol).

2.67) the products are almost entirely hydrogen, carbon monoxide, and silica.

At even richer fuel mixtures ($\Phi > 2.67$), carbon, rather than carbon monoxide, begins to be produced. Traces of silicon monoxide and silicon nitride are obtained as well and are shown at 10 x magnification. Carbon is produced and contributes to the typical yellow white color of these fuel-rich flames. This fuel-rich condition occurs in ordinary fires, as is shown in Figure 2.

Appreciable amounts of carbon are present to give the characteristic yellow color to the flame. The whitish color is caused by an abundance of silica of small particle size, which emits in the visible region. The flame temperature under these conditions is not particularly high (~1200°C) and is comparable to that of organic flames at similar fuel-to-air ratios.

An electron micrograph (Figure 6) shows gray tan amorphous silica particulates collected above the 50 cs polydimethylsiloxane fire shown in Figure 2. This is similar to particulates produced by a silicone rubber burning in air. The silica contains 3-4 percent total carbon, primarily elemental carbon, and 0.1-0.2 percent hydrogen. Amorphous rather than crystalline silica is always found in combustion of silicones. The amorphous silica consists of 100 A particles, tightly aggregated into 700-1000 A clumps, which are then further agglomerated in chains. Some larger particles, 2,000-4,000 A in diameter, visible near the top of the micrograph, appear to be carbon. They would account for the observed flame luminosity.

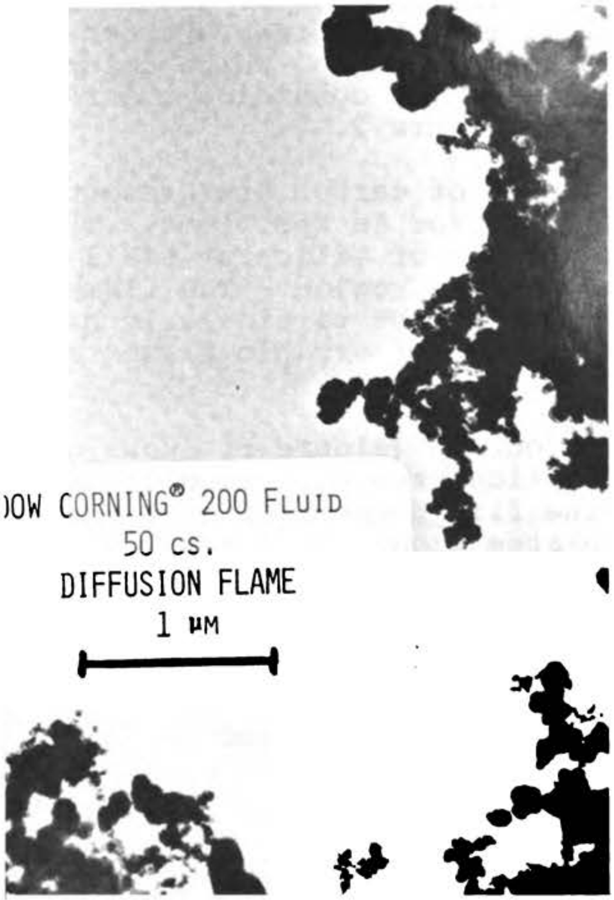
SILICONE WIRE AND CABLE INSULATION

The main criteria used in selection of insulation for wire and cable are as follows:

1. mechanical,
2. thermal,
3. electrical,
4. economic,
5. environmental, and
6. fire safety.

When materials for electrical cable use are being selected, mechanical, thermal, and electrical properties are

FIGURE 6. Particulates from Polydimethylsiloxane Burning in Air



of major importance. Reviews of these properties for silicone rubber wire and cable insulation are available (3, 5).

Economic considerations are of utmost importance as well. To consider total value to the user per unit cost is a more realistic approach to economics than to simply consider unit cost per pound.

Environmental considerations include effects of the environment on the insulation. Properties such as resistance to corona, radiation, ultraviolet light, ozone, moisture, steam, and various chemicals are important in some applications (3, 5).

The effect of the insulation on the environment is included in environmental effects. Toxicity effects on man as well as on other forms of life should be considered. No adverse environmental effects are known for silicone rubber. Their inertness in the body has led to a variety of devices that are widely used and approved for body implantation and have been so used for a number of years without adverse D_m effects. Furthermore, a number of polydimethylsiloxanes have received FDA approval for use in food processing and in various medicinals.

FIRE HAZARD PROPERTIES OF SILICONE RUBBER WIRE AND CABLE INSULATION

At the present time, newly developing concepts of fire hazards of sytems are replacing the narrower concept of flammability of materials. The characteristics that should be considered in assessment of fire hazard for electrical cable materials include ease of ignition; fire growth and flame spread; heat release; smoke and fire gases, including their identity and concentrations as well as their toxic and corrosive properties; oxygen depletion; fire endurance, which is the ability of the material to maintain physical and electrical integrity in a fire; and, finally, extinguishment behavior. I would like to cover each of these as it applies to electrical cable materials. The data have been selected to be representative and are not meant to be comprehensive. Data from both published literature and from within Dow Corning will be shown. Data for silicone rubber in some of these fire hazard categories are sketchy or nonexistent and will be indicated as such. On the other hand, data for silicone rubber on fire growth and flame spread are abundant. This abundance of data primarily covers the small-scale laboratory tests, including Limiting Oxygen Index, Underwriters Laboratory wire and cable tests (UL-62 and Subject 758), horizontal and vertical ASTM tests, and various aircraft materials' specifications. Flame retarded silicone rubber materials with Limiting Oxygen Indices of 30-40, which will meet the most stringent flammability requirements of these tests, are available.

The philosophy adopted in this presentation, though, will be that the most meaningful flame spread and fire growth tests are those most closely related to the conditions and scale of actual use. Therefore, these will be emphasized in this survey of fire hazard properties.

Table 1 shows ignition temperatures in degrees Celsius for some selected materials by the Setchkin ignition test (ASTM D-1929), which is a standard ignition test for solids. Piloted ignition (flash-ignition) and self-ignition temperatures for some common plastics, including polyethylene, poly(vinyl chloride), polytetrafluoroethylene, and several silicone materials, are given. Note that the silicones have self-ignition temperatures comparable to that of polytetrafluoroethylene. The self-igntion temperatures given for silicone rubber (480°-500°C) are based on a test generally used for fluids (ASTM D-286). Ignition temperatures by the Setchkin method are likely to be even higher than those found in the static D-286 method.

Table 2 shows fire growth and flame spread test data. Ignition of vertical cable trays was carried out using a 70,000-Btu/min ribbon-type gas burner as specified in IEEE Standard 383, covering Class 1-E electric cables for use in nuclear power generating stations (6). Complete cable constructions in vertical cable trays, using silicone rubber insulation, were subjected to 7-min ignition conditions with a ribbon burner. In all cases, vertical flame propagation, as shown by char area, stopped in less than 2 ft of the 8-ft vertical-cable-tray height. Burn times were 3 min or less after the flame was removed. The burner flame was then reapplied for 60 min without causing further flame propagation.

The maximum theoretical heat release of a burning material can be represented by its heat of combustion. Heat release in real fires is almost always lower than the theoretical heat of combustion because of incomplete combustion. Real fires usually produce carbon monoxide, smoke, and soot, which are products of incomplete combustion. Some heats of combustion, listed in units of kilocalories per gram for easy comparison, are shown in

TABLE 1

IGNITION TEMPERATURES OF SELECTED MATERIALS*

(ASTM D-1929)

MATERIAL	FLASH-IGNITION	SELF-IGNITION
POLYETHYLENE	340°C	350°C
POLYVINYLCHLORIDE	390	455
POLYTETRAFLUOROETHYLENE	--	530
SILICONE, GLASS LAMINATE	490	>500
SILICONE RUBBER	--	480-500°†

* C. J. HILADO, "FLAMMABILITY HANDBOOK FOR PLASTICS", 2ND. ED., TECHNOMIC PUB. CO., WESTPORT, CONN., 1974.

† ASTM D-286 AUTOIGNITION TEMPERATURE

TABLE 1 Ignition Temperatures of Selected Materials (ASTM D-1929)[a]

Material	Flash-Ignition °C	Self-Ignition °C
Polyethylene	340	350
Poly(vinyl chloride)	390	455
Polytetrafluoroethylene	---	530
Silicone		
Glass laminate	490	> 500
Silicone rubber	---	480-500[b]

[a] C. J. Hilado, Flammability Handbook for Plastics, Technomic Publishing Company, Westport, Conn., 1974.

[b] ASTM D-286 autoignition temperature.

TABLE 2 STD-383 Fire Test[a]

			7-min Ignition		
Cable	Insulation	Outer Cover	Afterburn (min)	Char Area (in.)	60-min Roast Propagation
A	Me_2 silicone	Asbestos	3.0	18	Pass
B	Me_2 silicone	Neoprene	0	16	Pass
C	5% PhMe silicone	Neoprene	3.0	17	Pass

[a] From reference (6). Vertical cable tray (3 in. by 12 in. by 8 ft) and ribbon gas burner (70,000 Btu/min).

Table 3. Polyethylene has a heat of combustion of 11.1 kcal/g, which is quite high. The heat of combustion for polydimethylsiloxane is 6.5 kcal/g. A typical silicone rubber wire and cable material, however, which contains 40 percent silica, has a heat of combustion of about 4 kcal/g. Poly(vinyl chloride) is comparable to this at 4.3 kcal/g. Polytetrafluoroethylene, on the other hand, combusts endothermically and thus requires a constant input of heat to maintain combustion.

The rate of heat release in actual fires, rather than total theoretical heat release, is more directly related to hazard. For example, 1 gal of gasoline and 7 lb of polyethylene have the same heat of combustion, but gasoline is far more hazardous because its heat of combustion is usually released much more rapidly. I know of no measurements of rates of heat release for silicone rubbers, though such data are available for pools of burning silicone fluids (2). For electrical cable materials, the geometrical arrangement of wire and cable as well as the ignition source used should directly affect the rate of heat release. Standardized heat release tests could be devised to provide comparisons between materials as well as to investigate the effect of various wire and cable arrays over a range of ignition energies.

Table 4 is taken from a National Bureau of Standards publication, Building Science Series 18 (1969). The publication shows smoke evolution data in the NBS smoke chamber for more than 150 materials under flaming (F) and nonflaming (N), or smoldering, conditions as well as maximum concentrations found for several common fire gases. Materials similar to wire and cable materials are shown. D is the maximum specific optical density reached in the smoke chamber and is a logarithmic measure of light obscuration. T_{16} is the time in minutes required to reach an optical smoke density of 16, which is considered to just cause physical obscuration of vision. Poly(vinyl chloride) has the highest smoke density and highest rate of smoke evolution of all the materials shown when corrected to a constant weight basis. Relatively high concentrations of carbon monoxide and hydrogen chloride are evolved. The fluoropolymer shown is a copolymer of tetrafluoroethylene and vinylidene fluoride. Its rate of smoke evolution and maximum optical density are among the lower of all listed materials shown in this table. However, the maximum concentrations of hydrogen fluoride are considerably above a dangerous concentration, which is considered to be 50 ppm. Chlorosulfonated polyethylene is intermediate in its rate of smoke evolution and its maximum optical density. Relatively high

TABLE 3 Selected Heats of Combustion[a]

Material	ΔH_c kcal/g
Polyethylene	-11.1
Polydimethylsiloxane	- 6.5[b]
Silicone rubber (40% SiO_2 filled)	- 3.9[b]
Poly(vinyl chloride)	- 4.3
Polytetrafluoroethylene	+ 0.08

[a] J. L. Throne and R. G. Griskey, Modern Plastics, McGraw-Hill, November 1972, p. 96.

[b] From reference (1).

TABLE 4 Smoke Characteristics
NFPA Test Method 258-T
National Bureau of Standards
Smoke Test Chamber[a]

Material	Weight, g	Exposure[b]	D_m	T_{16} (min)	Maximum Gas Concentration, ppm		
					CO	HCL	Others
PVC, plasticized	5	F	199	0.4	420	450	--
		N	180	1.4	500	450	--
Fluoropolymer $C_2F_4/C_2H_2F_2$	20.1	F	109	1.2	480	--	HF, 80
		N	75	2.5	20	--	HF, 90
Chlorosulfonated PE	16.7	F	230	0.8	750	400	SO_2, 50
		N	196	1.1	60	200	SO_2, 50
Chloroprene	18.8	F	233	0.7	550	200	--
		N	161	1.6	100	200	--
Silicone rubber	12.5	F	151	0.9	60	--	--
		N	44	2.8	10	--	--

[a] National Bureau of Standards, Building Science Series 18, 1969.

[b] F indicates flaming; N indicates nonflaming.

concentrations of hydrogen chloride and sulfur dioxide are emitted under both flaming and nonflaming conditions. Chloroprene represents intermediate rates of smoke evolution and specific optical density. However, high concentrations of carbon monoxide and hydrogen chloride are produced. The silicone rubber represents intermediate rates of smoke evolution and specific optical density under flaming conditions and low rates of smoke evolution and maximum specific optical density under smoldering conditions. Only low levels of carbon monoxide were identified in the monitored gases. This is consistent with the data shown earlier on combustion products of polydimethylsiloxane, in which carbon monoxide, carbon dioxide, and water are produced as gases. Amorphous silica particulates are also produced. A toxic gas that may be emitted from silicones under smoldering conditions is formaldehyde, which was not monitored in this NBS study.

In some electrical cable installations, corrosive properties of evolved smoke and gases may be of more concern than toxicity. Vapors from heated dimethyl silicone rubber cable insulation showed the lowest corrosivity to copper of all wire and cable materials tested in the Copper Mirror Corrosion test (ASTM D-2671) (7).

Table 5 shows National Bureau of Standards Smoke Chamber data obtained under flaming conditions for a typical dimethylsilicone rubber and for flame-retarded dimethyl and phenylmethylsilicone rubbers. Note that smoke-particulate evolution is reduced for the flame-retarded rubbers as compared to the standard rubber. The flame retardants used in Dow Corning silicone rubbers consist of very low levels of non-volatile metallic compounds. These metallic flame retardants work by causing massive crosslinking at high temperature, which minimizes the evolution of flammable cyclic siloxanes. Evolution of smoke particulates from these flame-retarded silicone rubbers is considerably reduced in comparison to the standard rubber. Some gaseous products are released in the crosslinking reactions; these include hydrogen, methane, and other low-molecular-weight hydrocarbons, shown as HC in the table. These gases are low in toxicity and corrosivity.

Many organic materials contain halogenated flame retardants, halogen-antimony combinations, or phosphorous or nitrogen flame retardants. These elements may be incorporated in the polymer structure. The presence of these elements often causes increases in the rate of smoke evolution and increases in the maximum specific optical density. Halogens, P, N, and Sb also tend to increase the toxicity and corrosive character of the smoke and fire gases as well. We are currently carrying out an extensive series of animal exposure tests by subjecting animals to the smoke and vapors from silicone rubber materials, both standard and flame-retardant types. These animal exposure tests are being conducted under a number of conditions in both flaming and smoldering modes.

Figure 7 shows thermogravimetric analysis curves for the standard dimethyl rubber and for the flame-retardant material shown in Table 5. Percent weight remaining is plotted against temperature for these rubber samples, which were heated at a 10°C per min heating rate in nitrogen. Both materials begin to lose weight at about 300°C, which represents loss of the small amount of low-molecular-weight materials present in the cured rubbers. Note that the flame-retarded rubber has lost only 14 percent of its weight above 900°C, whereas the standard rubber has lost 62 percent of its weight. The 62 percent weight loss represents all of the polydimethylsiloxane content originally present. The crosslinking effect of the metal compounds used in the flame-retarded rubber is readily apparent.

A relevant test for fire endurance of electrical cable materials is the determination of electrical insulating properties after exposure to fire. In one simple test, a cable bundle is arranged as shown in Figure 8. Current flow between adjacent cables will complete the circuit and energize the light bulb. Exposure to a Fisher laboratory burner does not cause loss of insulating ability in more than 30 min for the FR silicone rubber-insulated cables. However, poly(vinyl chloride) and fluorocarbon insulations lose their insulating ability in 1.5 to 3 min of exposure to the flame.

A more sophisticated test for cable designs was described by Noble (6), using IEEE Standard 383 fire tests described earlier for class 1-E electric cables (Table 6). Portions of cables exposed to the ribbon burner for 1 hour were tested for their insulation resistance. Cables were first bent around a 12-in. mandrel and then given a reverse bend around another mandrel and tested. Ranges of insulation resistance in Mohms per 1000 ft are shown for six cable samples. Cables were also tested for AC-dielectric-withstand strength for 1 min at 1,000 and 4,000 V. All cables withstood 1,000 V, and some specimens were able to withstand 4,000 V.

The final two criteria of fire hazard are oxygen depletion and ease of extinguishment. I know of no data on

TABLE 5 NBS Smoke Chamber (Flaming) Data for Silicone Rubber (3.3-mm Thickness)

Sample	D_m	T_{16} (min)	Gas Analysis			
			CH_4 (ppm)	CO (ppm)	HC (ppm)	CO_2 %
Me_2 rubber	436	1.2	None	130	48	1.36
Me_2 rubber (flame retarded)	119	1.5	220	160	279	1.09
PhMe rubber (flame retarded)	70	1.9	320	150	217	1.06

TABLE 6 Electrical Data For Six Cable Samples After Fire Test[a]

Cable	Insulation	Insulation Resistance (Mohm/1000 ft)		Dielectric Withstand Strength[b]	
		After Roasting	After Bending	1000 V	4000 V
A	Silicone	29-252	30-300	6	5
B	Silicone	0.9-144	0.2-135	6	0
C	Silicone	5-135	8-126	6	3

[a] From reference (6).

[b] Number passing of six samples tested.

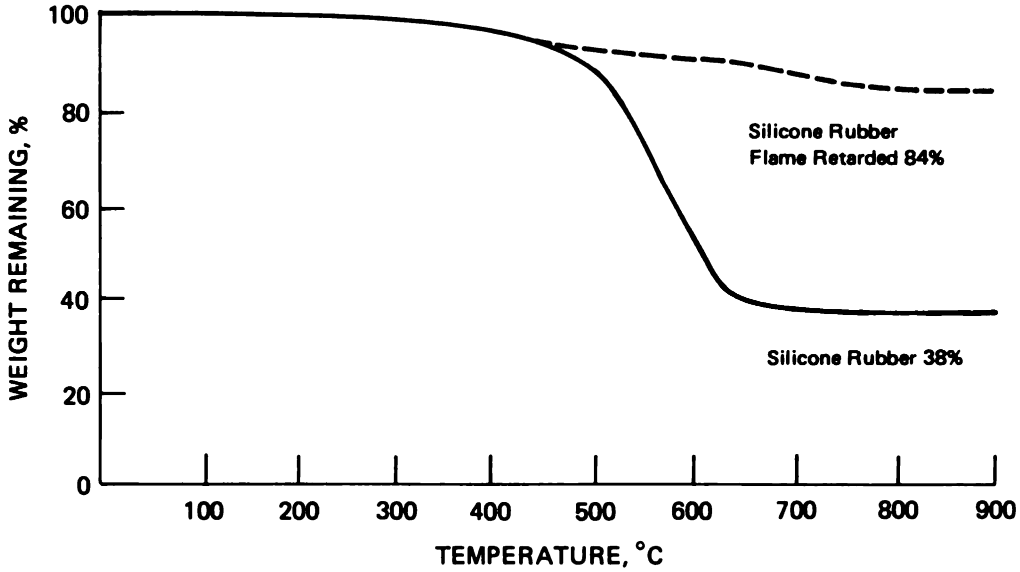


FIGURE 7 Thermogravimetric analysis (10°C per min in N_2).

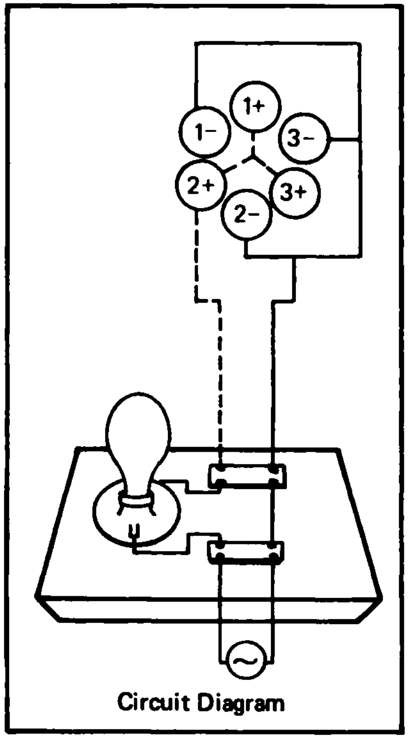


FIGURE 8 Electrical integrity test (Fisher burner flame test).

Material	Flame Propagation	Time to Circuit Failure
Silicone rubber (flame retarded)	No	>30 min
PVC, fluorocarbons	No	1.5–3 min

silicone rubber for either. Oxygen depletion is primarily of interest for materials used in large volumes in enclosed areas in which oxygen depletion can be a life hazard. This is not generally the case with wire and cable insulating materials, though it may be important in some situations. Although ease of extinguishment of silicone rubber has not been studied, we have looked extensively at extinguishment of high molecular weight polydimethylsiloxane fluids (2). These fluids are readily extinguished with carbon dioxide or dry chemical extinguishers as well as water sprays and water sprinkler systems. The silicone rubbers should behave similarly.

Finally, two silicone materials contribute to a fire-safety package when used in conjunction with flame-retarded silicone rubber cable insulation. Sylgard 170 is a flame-retarded room-temperature vulcanizing material. It is easily applied, cures rapidly, and can be used to seal splices and connectors in cable installations. It has similar performance properties and fire hazard properties to the flame retarded silicone rubbers and has a flammability rating of V-O in UL Standard 94.

Dow Corning 3-6548 is a flame-retarded, room-temperature vulcanizing foam, ideal for preparing fire stops and penetration seals. It is easily applied and is recommended for use in wall, ceiling, and floor openings up to a size of 4 ft x 4 ft. There it serves as a barrier to flame and smoke penetration at points where conduits and cable trays pass through partitions. This material provides up to 3 hours of protection in the ASTM E-119 Furnace Test Standard, giving protection to a temperature of 2,000°F. It has an E-84 flame-spread rating of 20 and is specified in a number of new nuclear plant installations, many of which are currently under construction.

To summarize then, the silicone wire and cable insulating materials provide a good combination of fire-safety and performance properties. These silicone rubbers and sealants, especially the flame-retarded types, should be considered in installations for which fire safety is an important consideration.

ACKNOWLEDGMENTS

I thank my colleagues George A. Gant and Ronald M. Fraleigh for their valuable suggestions and contributions of data to this paper.

REFERENCES

1. J. Lipowitz. J. Fire Flammability 7:482, 1976.
2. J. Lipowitz, and M. J. Ziemelis. J. Fire Flammability 7:504, 1976.
3. K. E. Polmanteer. J. Elastoplast. 2:165, 1970; W. J. Bobear. In Rubber Technology, 2nd ed., M. Morton, ed., Van Nostrand Reinhold Company, New York, Chapter 15.
4. D. R. Stull. Chem. Eng. Prog., Loss Prev. 4:16, 1969.
5. E. C. Elliott, and J. W. Swanson. Paper 75CH1014-0-EI-26, presented at Twelfth Electrical/Electronics Insulation Conference, Boston, 1975.
6. M. G. Noble. Off. Plast. Caoutch. 22: 693, 1975.
7. J. W. Robertson. Paper C74 207-7, presented at IEEE Winter Meeting, New York, January, 1974.

Workshop Summaries

TESTING FOR FLAMMABILITY, SMOKE, AND CORROSIVE GASES

Louis J. Frisco
Raychem Corporation, Menlo Park, California

The workshop on Flammability, Smoke, and Corosive Gases was well attended and took place over a period of several hours, so it is only possible to present the highlights. Since the subject matter is complex and somewhat controversial, the salient arguments are presented without regard for the reporter's personal opinions.

FLAMMABILITY TESTING

The vertical-tray, cable-flammability test described in IEEE Standard 383, (IEEE Standard for Type Test of Class 1E Electric Cables, Field Splices, and Connections for Nuclear Power Generating Stations) was discussed extensively. It was apparent that this test is not universally accepted as the ultimate test in large-scale fire testing of cables, but it is being widely used and is, perhaps, the best tool generally available. It has been recommended for inclusion in MIL-C-915, (General Specifications for Cable and Cord Electrical, for Shipboard Use), which covers Navy shipboard cables. It will also be included in a revision of IEEE Standard 45 (IEEE Recommended Practice for Electric Installations on Shipboard), which will be available in the near future from the IEEE Publications Department.

Representatives of insurance underwriters who are concerned with Class 1E cable applications in nuclear power generating stations reported that extensive flammability testing has been conducted at Underwriters'Laboratory in Northbrook, Illinois. As a result they will require that their clients include in their specifications a modified IEEE 383 test with increased flame intensity (210,000 Btu/hour) and the addition of a "corner" in the test configuration.

The Tunnel Test was also discussed with much interest. This test had been described earlier in the program in a paper presented by Stanley Kaufman. There is some interest in the test as a means of evaluating smoke particulate emission, as well as flammability. However, major modification of existing equipment would be required to accommodate large, heavy cables. Comments regarding smoke emission measurements during tunnel tests are given below. Considerable concern was expressed regarding the cost of tunnel testing and the lack of available tunnels in the cable industry.

There seemed to be general agreement that large-scale tests are required for the purpose of establishing the suitability of a product for use in a particular application, but small-scale tests are needed for the purpose of monitoring performance on a production-lot basis as part of quality assurance programs. Better correlation is needed, however, between large-scale and small-scale test results, but the purpose of each type of test should not be confused. It was also pointed out that the Nuclear Regulatory Commission has issued an RFQ for a study directed at the correlation of large-scale cable testing and the events occurring in an actual fire situation. It was reported that the study will take about 30 months to complete.

SMOKE EMISSION TESTING

It was generally agreed that the NBS Smoke Density Chamber and other small-scale smoke density measuring devices serve a useful purpose in materials-development programs. They also have a place in quality assurance tests designed to assure the uniformity of insulating compounds on a production lot basis. However, a need was expressed for larger-scale tests that more closely simulate conditions that can occur in a fire situation.

The Tunnel Test is being considered by some researchers as a means of measuring smoke density. Additional instrumentation is required, and a great deal of work will have to be done to determine the effects of altering test parameters, for example, airflow rate, burner intensity, cable packing density, etc.

The Navy is considering the extension of the IEEE 383 test to provide data on smoke density. For such a test to become a standard, it will probably be necessary to more precisely define the size and configuration of the flame chamber (room). Work will be done at the David Taylor Naval Ships Research and Development Center, Annapolis, Maryland in an attempt to instrument the IEEE 383 test to provide smoke density data pertinent to shipboard cable installations.

Several participants pointed out that smoke emission characteristics are not necessarily predictable from a knowledge of the component materials in cable construction. Actual smoke emission, in terms of optical density and chemical composition, depends on the environment in which the cable finds itself in a fire situation, the design of the cable, and the design of the cable installation. These comments support the general concern that large-scale tests must be developed to provide meaningful data on smoke emission behavior.

CORROSIVE GASES TESTING

Not a great deal was said about testing for corrosive gases in products of combustion. It was reported that the IEEE Insulated Conductors Committee, Working Group 12-36, is beginning work on adapating the IEEE 383 test to determinations of quantities of corrosive gases generated during the standard vertical-tray flammability test. Apparently, the approach will be to determine the weight loss during the flammability test and then, from the known composition of the cable insulation and jacket, to calculate the quantity of acid gas generated. A large amount of work will be required to determine whether this approach yields meaningful results.

GENERAL REMARKS

Several comments were made concerning the costs of large-scale testing and the need to develop small-scale tests for routine testing to ensure uniform quality. In the final analysis, the search for ideal cable insulating materials and the methods of testing cable installations must yield products and economically viable installations. In a few critical applictions, cost may be no object, but that will not be the case for most applications. Additionally, a cable must be designed to exhibit the right balance of properties in order to perform its intended function in each application. Regardless of the importance of flammability, smoke emission, and gas generation, a cable must also possess satisfactory electrical and physical properties under operating conditions or it may cause a catastrophic failure that initiates a conflagration. In the near term, emphasis will be placed on the design of cable installations to minimize fire spread and to facilitate early fire detection and control.

TOXICOLOGY

Herbert H. Cornish
University of Michigan, Ann Arbor, Michigan

There was general agreement among those present that toxicity testing procedures for thermal decomposition products of natural and synthetic polymers are still in the developmental stage. Different groups of investigators are utilizing a variety of exposure techniques, various methods of thermal decomposition, several types of chambers, and a wide choice of biological measurements for evaluating effects on experimental animals. Out of these early investigations has come the diversity of toxicological data that presently exists. Although most investigators may be able to obtain rather reproducible results with their own particular system, how their data correlate with other techniques, and how any single procedure correlates with an actual end-use fire situation, have not been clearly defined. In fact, the end uses of polymeric materials are so varied, and fire situations so unique, that a standard fire situation appropriate to all end uses of materials is extremely difficult to develop, and compromise techniques must ultimately be accepted. During this developmental period we are attempting to assess the effects of variables on the toxic response and, at the same time, are making some attempts to compare natural and synthetic materials.

With respect to the end points in toxicity testing, those being utilized include mortality, time to incapacitation, and behavioral techniques. It was pointed out that in a number of studies using primates during exposure to irritants and other gases, animals would continue to perform in avoidance-response modes until very near death. Thus, even these types of responses may be difficult to investigate in a manner that will provide meaningful and sensitive results in the area of fire toxicology.

With regard to the specific end uses of materials, it appears that one of the major concerns with respect to naval problems would be flame spread. Flame spread may be more critical than the acute toxicity of combustion products, since it is essential that the fire be contained. In addition, for certain critical wiring situations, the major concern is the circuit integrity necessary to keep a ship functional. Thus, these specific requirements may well determine the relative importance of ease of ignition, flame spread, and toxicological data. It was suggested that because relatively few documented data are available on man and his response to fire situations, shipboard fires might provide such data because all personnel involved would be readily available. It was reported that, in actual fire situations where firemen and other individuals were exposed to HCl from poly(vinyl chloride), the sensory response to HCl appeared to be rapidly lost; continued exposure with little awareness on the part of the individuals involved resulted. Thus, the human detection system may also fail at a very crucial time.

Further discussion was related to the importance of the rate of burning, as well as the amount combusted, to toxicity testing procedures. The use of fire retardants to prevent flame spread is an important safety consideration, even though they may alter or even contribute to the overall toxicity of the combustion products. It was suggested that, in some instances, there may be increased smoke-particulate production from fire-retarded materials, although this effect does not occur with all fire-retarded materials. The mode of combustion, flaming or nonflaming, is also important in smoke production with or without the presence of flame retardants in the polymer. Smoke obscuration is an important factor in fires and can be quantified in testing procedures, but it is difficult to incorporate or relate smoke obscuration to toxicity testing. Yet, the role of particulate matter is of importance from a toxicological viewpoint both with respect to particulate blockage of the bronchioles and to the adsorption of water-soluble toxic gases on the particulate surface, which may then carry the irritant gas into the alveoli of the lung.

There was general agreement that although the immediate concern is for an individual's ability to survive and escape from a real fire situation, test animals should be maintained and observed for 1 to 2 weeks after testing to allow for the development of delayed effects, which may be just as life-threatening as is the more immediate response. This is an area of study that should, perhaps, be further developed to include an even longer observation period after a severe fire-exposure situation.

With the present state of the art, it appears that fire toxicity testing alone will not allow for fire discrimination in the selection of "safe" versus "unsafe" polymers. We should, however, be able to pinpoint those materials that present an unusual hazard from a toxicological viewpoint. Thus, the "screening" toxicity data developed for individual polymers must be used along with other available test data for an overall assessment of the hazard involved in a real fire situation.

The National Academy of Sciences is in the process of developing guidelines for fire toxicity testing procedures that will help to define in more detail some of the problems discussed at this meeting. In addition, its report will also offer suggestions on the development and appropriate use of toxicity test data in an evaluation of the hazards resulting from the combustion of polymeric materials.

ADVANCED MATERIALS AND DESIGN

Joseph R. Perkins
E. I. DuPont de Nemours and Company, Wilmington, Delaware

ADVANCED MATERIALS

More work has been done in modifying conventional materials to reduce their flammability than in developing new materials. These materials are PVC, polyethylene, and various rubbers. Since the Brown's Ferry fire and the advent of the IEEE 383 test procedure, such materials have been modified by additives in order to make them capable of passing the 383 test. This kind of modification applies also to the silicone rubbers. Fluoropolymers are inherently flame retardant and are capable of passing the 383 test without modification. The additives used are halogens, phosphorus-type materials, and alumina with various other materials such as antimony compounds, which work synergistically with the halogens.

David Tate, assistant director of research for Firestone, gave a report of their work on polyphosphazenes, a new series of polymers developed partly under a Navy contract. An outline of this report is given in Appendix A.

Uniroyal briefly reported an unidentified and trade name compound during the last Wire and Cable Symposium at Cherry Hill, New Jersey. It passes the 383 test, has an Oxygen Index in the range of 28 to 35, and may find utility in the area of flame-retardant insulations.

The question was raised concerning what quantity of experimental polymer is needed for the development of new wire and cable products. For a single evaluation by a given manufacturer, a minimum of 50 lb would probably be required for a single run in a wire and cable mill. A complete evaluation of a new wire or cable product would take much more than this amount. Moreover, if the evaluation were industry wide, tons of materials would be required.

It was further inferred from experience that insulating materials for wire and cable can be produced economically only if there is a major market for the materials in other areas of application because the quantities used for wire and cable are not large enough on a comparative basis. Thus, wire and cable insulations developed for that specific purpose will be inherently expensive.

DESIGN OF CABLES

Cable design involves consideration of the materials that enter into its construction, the way those materials are used, and the methods of cable installation as a part of the overall design when flammability and products of combustion are of concern.

In considering a cable design, it is necessary to distinguish between the requirements of circuit integrity and flame propagation. These are two independent properties. A cable can maintain electrical insulation between parts of a circuit while the flame propagates along its length.

To produce circuit integrity requires no new technology. It is only necessary to interpose an inorganic insulating material between the conductors in addition to other coverings. A conventional way of insulating cable is to wrap mica tape over a conductor and then extrude an insulation over it. Another way to protect a cable is to extrude an insulation around the conductor and put a glass braid over it. Mica tape over insulation usually does not work because the expansion of the insulation when heated can burst the tape.

Because any organic insulation can be made to burn under certain conditions, design of the installation is of great importance. It is essential that the installation of a cable discourage the propagation of fire. In evaluating a particular installation in regard to the danger of propagation of fire, it is helpful to review the essential factors involved in the burning process and consider each of them when inspecting the design. These factors are as follows:

1. Ignition source. The ignition source is a a source of heat that produces chemical cracking or destructive distillation of the covering materials, which in turn produces flammable off-gases.

2. Off-gases. Although produced by heat from an ignition source, off-gases must be exposed to the right amount of oxygen in order to burn. If there is too low or too high a percentage of such gases in the air, the mixture will not ignite. Moreover, there must be a sufficiently high temperature or a flame present to ignite whatever flammable mixture there may be.

3. Regeneration or feedback. For flame propagation, the burning off-gases must heat the cable covering to generate additional gas adjacent to the ignition source. If insufficient heat is generated, the fire will extinguish once the ignition source has been removed.

Intumescent paint over a cable protects it from the heat of the ignition source, thereby causing a delay in the generation of flammable off-gases until the ignition source fire can be extinguished. A fire lasting indefinitely will heat flammable insulation under an intumescent paint and cause the generation of gases that will break through the intumescent paint and burn. Thus, the use of an intumescent barrier material constitutes a delaying tactic.

On the other hand, use of a closed vertical tray open at the top and bottom is a chimney. Then, almost any combination of insulations can be made to burn where there is adequate draft.

A closed tray, with a fire stop at the top, will prevent flame propagation even if the tray is leaking off-gases generated at the bottom where there is an igniting source that will fill the tray to the point where a nonflammable mixture is present. An initial flash may occur when the mixture becomes combustible, but thereafter a combination of flammable gases and nitrogen, which is nonflammable, will coexist. In this regard, it is well to remember that fires usually operate in a dearth of oxygen. Oxygen is often consumed faster than it can be replaced under equilibrium conditions, and higher temperatures usually reduce the oxygen concentration present, but these circumstances do not extinguish the flame.

SPRINKLER SYSTEMS

Fire protection people in the construction industry favor sprinkler systems, which have a remarkable record of performance in preventing disastrous fires. Yet, electrical users are understandably worried about water where there are exposed terminals. This concern does not mean that wiring cannot be designed so that a sprinkler operating above it will not cause trouble, but it is more expensive. We can expect to see more use of sprinklers in critical electrical applications because of pressure by insurance people and, in the case of nuclear plants, the Nuclear Regulatory Commission.

Despite their importance, hazards such as smoke, toxicity, and corrosion by-products in a fire feeding on burning electrical insulation represent only a small part of the problem of the performance of wire and cable coverings. The major purpose of wire and cable insulations is to provide reliable insulation service over the time and temperature requirements of the design. It must do this or else the wire and cables will not be functional.

PROPERTIES OR REQUIREMENTS OF WIRE AND CABLE COVERINGS IN ORDER OF IMPORTANCE

Mechanical

Wire covering must be sufficiently strong to be pulled into place and withstand any vibration, expansion and contraction, or mechanical shocks during the entire life of the installation. If the material is not sufficiently strong to be installed, there is no point in considering the other properties of the material.

Thermal

Coverings must be capable of withstanding the normal design operating temperature for the required life of the plant without mechanical deterioration. In addition, it must be capable of withstanding short-term exposures because of overloads or other deleterious conditions that may arise. Because the thermal and mechanical properties of insulation are interrelated, the mechanical properties must not decrease with use temperatures to the point that makes a wire or cable useless.

Environmental

This is a double-ended requirement. The environment must not cause degradation of the wire and cable coverings. Conversely, the wire or cable must not introduce adverse environmental effects such as the corrosion of adjacent metals. Solvents, oils, alkalies, and other chemicals are typical concerns. Fire, as a possible environmental danger, must always be considered in installation design.

Electrical

While most people consider electrical properties first, they are usually of least importance because if an insulating material is mechanically, thermally, and environmentally suitable, it is almost always electrically suitable.

Economics

Wire and cable materials should be selected to meet the necessary performance requirements at minimum cost. A part of such value analysis is the hazards analysis associated with the effects of fire on the insulating materials.

RETROFIT OF NUCLEAR POWER PLANTS

Approximately 60 plants are getting some degree of retrofitting to eliminate possible fire hazards. As a result of a requirement by the Nuclear Regulatory Commission, the National Research Council has a contract with the Sandia Corporation to develop some basic engineering information with respect to fire in wiring systems that will be of help in designing the best retrofit procedures.

FUTURE DESIGN

An obvious technique for reducing fire hazard is to restrict the amount of fuel available in the form of wire and cable coverings. One way of reducing the amount of covering materials is to use smaller diameter wire and cables, because in many instances the conductor sizes are much larger than are needed for electrical requirements. With the development of solid state technology, the need for presently used power levels in control equipment can be largely reduced and enable the wiring to be smaller. Another positive factor is to use insulating materials that yield lower heats of combustion per unit volume than do those in currently used materials. Thus, use of a small-diameter wire with a thin- walled low British thermal unit per unit volume insulation will give a greatly reduced fuel load for a fire. One recent example using this technique has reduced the available fuel in a particular design for a large instrumentation system by approximately 90 percent.

DETECTION OF FIRES IN ELECTRICAL CABLES

Richard Bukowski
National Bureau of Standards, Washington, D.C.

Probably the most significant conclusion determined during the discussion is that there is no single answer to the problem. Fire detection, alarm, and extinguishment must be designed to the specific hazard to be protected in order to optimize both the operational effectiveness and economics of the system.

As an analogy, consider the hammer. The hammer is a tool typically used to drive nails, but there are different types of hammers; claw, ball peen, dry wall, tack hammers, sledgehammers, etc. Each has a specific purpose. The amateur carpenter may have only one hammer to use for all purposes. But the professional has many different types and uses all in the way in which they are intended. Likewise, there are many types of fire detection devices, and a sign of the professional is the use of each in its optimum configuration.

The best intervention strategy is to prevent a fire or at least limit its magnitude through the use of better cable insulations. If these means are not possible, then a detection system must be designed to provide early warning for the purpose of extinguishing the fire before significant damage can occur. When designing such a fire alarm system, the following points should be considered.

1. The first consideration should be the risk. The amount of risk will affect the decision on the speed of detection necessary. For low risk situations, slower, more economical detection can be used. One example of this situation might be a cable tray containing cables carrying power to the water coolers within a building. If a fire destroyed these cables, the only consequence might be warm drinking water. For this case, one might consider the use of a line-type heat sensor, which is quite economical and

easy to install and maintain. The purpose of this type of detection is primarily to prevent structural damage to the building and to limit the amount of cable replacement after the fire.

As the risk increases, one may wish to go to smoke detection at standard spacings, smoke detection at reduced spacings, or the mixing of detection types to increase the speed of detection and amount of discrimination against false alarms inherent in the overall system.

2. The second consideration is the type of fire risk prevailing. Specifically with regard to electric cable fires, there are two types of risks that might be encountered. These are external exposure of the cable to a fire originating in other combustible materials or internal over-heating due to overloads or short circuits in power cables. These two types of fire risks can be encountered singly or in combination. For example, limited energy signal cables may only have an external exposure problem, and power cables that are run through concrete tunnels where no combustibles are stored may have only internal exposure possibilities. However, power cables that are run above a suspended ceiling may have both. The type of fire exposure will affect the decision on the type of detection device used because each different type of exposure may produce different signatures. Where the cables being protected are vital to the operation of a facility, one may wish to detect the early pyrolysis products from the decomposition of insulation. Conversely, where the risk is low, and false alarms could be a problem, one may opt to accept slower detection and wait for open flaming.

3. The third decision point is the consideration of the materials being protected. One should look at the expected fire signatures released from the specific materials involved when exposed to the risk as defined above. For example, poly(vinyl chloride) insulation under low-temperature breakdown, applied in a vital system function requiring rapid detection, may lead one to use photoelectric smoke detection, which reponds to the early pyrolysis products given off under low-temperature conditions. Specifically, this detectable substance is a white, hydrogen chloride fog containing no solid particulates.

4. The fourth point involves the conditions normally expected in the protected spaces. Such conditions might be airflow patterns, temperature, and humidity or may involve other equipment and processes that may generate products to

which the detectors selected are sensitive. Because the product to be detected must be transported to the detector before an alarm can be effected, the airflow patterns have great impact on detector placement. In fact, in very still spaces such as unventilated cable tunnels, one might even want to provide forced airflow to assist the combustion products in reaching the detector. Also, where low-thermal-energy fires or high humidities may be encountered, the combustion products often hang low in the protected space. Thus, one might want to place the detectors low within that space.

With regard to background processes one may wish to use signal discrimination through reduced sensitivity, multiple detection modes, or such system connection parameters as cross zoning or priority matrix. These system parameters require the alarm of two detectors on different zones or in adjacent installations. Such systems can be used to provide a presignal on the first alarm but withhold a general alarm, notification of the fire department, or automatic release of an extinguishing agent, until the second detector alarm actuates.

A part of this decision is the consideration of detection speed as a function of risk. Where vital system function is involved, one may want to allow a certain number of false alarms to increase the overall detection speed in case of fire. It is also necessary to consider the amount of damage one could sustain from a fire. This judgment would affect the detection speed consideration.

5. The next consideration is what happens when the alarm occurs. An automatic detector can only notify someone that a fire exists. This notification should be coupled with manual or automatic extinguishment. The use of automatic extinguishment usually involves the need for more discrimination because the extinguishing agents are often costly or can, themselves, cause damage to a protected area. But, additional discrimination often sacrifices some detection speed. As was mentioned earlier, use of prenotification on the first alarm with cross-zone or priority-matrix-type installations can minimize the sacrifice in detection speed while still providing the discrimination necessary for automatic extinguishment.

Manual estinguishment also increases the need for detection speed because it takes a finite time to begin the extinguishment process. Further, the use of manual extinguishment may necessitate a high degree of zoning to allow immediate pinpointing of the precise fire area. For example, if all detectors on one floor of a large building are in the same zone, it is quite difficult to pinpoint the fire other than locating it on the given floor. If, however, the floor is subdivided into a number of zones, the areas that have to be searched to locate the fire are reduced. Additionally, the extinguishing agent to be used on the fire should always be proved for the material involved and the type of fire expected.

6. A final consideration involves the design priorities. If one has a choice between a cable with low flammability (but which produces a fire that is hard to detect once ignited) or a second cable with higher flammability (but which is easier to detect once ignited), one should always choose the low-flammability cable and use proper systems engineering to provide for specific detection needs. This procedure may involve modification of existing detection equipment or possibly even the development of new detection equipment. One should always be able to devise a detector that will do the job, but doing so may involve exotic detection schemes such as chemical "tags" incorporated in the insulation, coupled with special detectors that sense this chemical tag released upon heating. Also, we are entering into the era of the "smart detector." In the next few years, detectors may provide analog readings to computers or contain individual microprocessors that can make decisions based on the signal strength, rates of change, or other parameters. Such smart detectors should increase detection speed for real fires and decrease false alarms.

The key point of the entire discussion is that the intelligent application of a systems design approach is necessary to provide the level of detection performance one requires at a cost consistent with the risk involved. As for the hammer analogy, each and every type of detector and system available has applications where it and it alone is the best. The answer to the question of what detector and system arrangement are necessary must be determined through a logical decision process. This process should always involve a qualified fire protection engineer or system designer who is familiar with all types of detection equipment and the ways in which each works the best.

Appendix

PHOSPHAZENE POLYMERS: POTENTIAL JACKET AND INSULATION MATERIALS FOR ELECTRICAL CABLES

David P. Tate
Firestone Tire and Rubber Company, Akron, Ohio

I. Introduction

A. The phosphazene polymers form a generic class of compounds. By the proper choice of pendant group and molecular weight one can obtain materials exhibiting the entire range of properties typical of high polymers. Hard crystalline plastics, amorphous rubbers, resins, oils, fibers, films, etc., have all been prepared.

B. Two phosphazene polymers have shown commercial promise, and production has been scaled up in a pilot plant at Firestore Central Research Laboratory.

1. Fluoroalkoxy pendant groups.
    - Developed for oil-resistant rubber goods application.
    - Low flammability but high halogen content. May give toxic combustion products.
    - High-cost raw materials.
2. Aryloxy (phenolic) pendant groups.
    - Low-cost raw materials.
    - Low smoke and toxic gas evolution as well as low flammability.

II. Fluoroalkoxy-Type Polyphosphazene (PNF-200)

A. PNF-200 vulcanizate has typical rubber processing and stress-strain characteristics.

B. Insulating properties are fair to good.

C. Flammability of vulcanizate is low.

D. A brittle nonconductive ceramic-like char is formed on pyrolysis in a flame.

III. Aryloxy-Type Polyphosphazene (APN)

A. Early work was done by Horizons, Inc., under Navy and NASA contracts.

B. Armstrong published flammability and smoke data.

1. Foam rubber.
    - Thermal insulation.
    - Comfort cushioning.
2. Cable jacketing.

C. Firestone is currently developing foam rubber comfort cushioning based on this technology. The early data of Horizons on low smoke and flammability was confirmed, and improvements in the processing and cure systems have been made. In addition, preliminary animal and analytical test data lead us to believe that the products of combustion of APN have a very low level of toxicity. The lack of definitive protocol for animal testing of combustion products causes us to be cautious in assessing its toxicity, but preliminary tests look quite encouraging.

D. Applications as cable jacketing and paint coating are natural extensions of this technology.

- Conventional processing.
- Low cost raw materials.
- Low smoke.
- Low toxicity.
- Low flammability.
- Developmental quantities available in late 1977.

ROSTER OF PARTICIPANTS

BERNARD G. ACHHAMMER, NASA Headquarters, Washington, D. C.

DOMINICA A. ALIA, Phelps Dodge Cable and Wire Company, Yonkers, N. Y.

DAVID B. ALLEN, E. I. DuPont deNemours and Company, Wilmington, Del.

ALAN S. AMBROSE, B. F. Goodrich Chemical Company, Cleveland, Ohio

JAMES J. ANASTASI, Brand-Rex Company, Willimantic, Conn.

FLOYD E. ANDERSON, Naval Ships Engineering Center, Washington, D. C.

HENRY APFELBAUM, Bell Laboratories, Murray Hill, N. J.

STANLEY M. BARKIN, National Academy of Sciences, Washington, D. C.

R. H. BARTON, E. I. DuPont de Nemours, Wilmington, Del.

PAUL D. BASCONI, The Kerite Company, Seymour, Conn.

JESSE J. BEITEL, Southwest Research Institute, San Antonio, Tex.

CHARLES BENDERSKY, Private Consultant, Basking Ridge, N. J.

E. W. BENNETT, JR., ITT Surprenant Division, Clinton, Mass.

DONALD BENOIT, Wire and Cable Corporation, Leominster, Mass.

WALTER BERL, The Johns Hopkins University, Laurel, Md.

WILLIAM I. BLAZEK, General Services Administration, Washington, D. C.

HARRY N. BOCKUS, Jr., Solar Compounds Corporation, Linden, N. J.

CHARLES BOGNER, NAVSEC, Washington, D. C.

STANLEY BORONSKI, Great American Chemical Corporation, Fitchburg, Mass.

JOSEPH A. BRADLEY, JR., Tennessee Valley Authority, Knoxville, Tenn.

RICHARD G. BRIGHT, National Bureau of Standards, Washington, D. C.

J. L. BRODSKY, Plastoid Corporation, Hamburg, N. J.

GEORGE S. BUETTNER, The Rockbestos Company, New Haven, Conn.

RICHARD W. BUKOWSKI, National Bureau of Standards, Washington, D. C.

JOSEPH T. CALLAHAN, NAVSEC, Philadelphia, Pa.

HOMER W. CARHART, Naval Research Laboratory, Washington, D. C.

PETER CARSON, Raychem Corporation, Menlo Park, Calif.

NICHOLAS CHERGOTIS, Pyrotronics, Inc., Cedar Knolls, N. J.

ROGER R. CHOLIN, Firetek Corporation, Clifton, N. J.

W. J. CHRISTIAN, Underwriters Laboratories, Inc., Northbrook, Ill

WALTER M. CINIBULK, Raychem Corporation, Arlington, Va.

RICHARD J. COLLINS, ITT Surprenant Division, Clinton, Mass.

WALTER F. CONSTANTINE, Collyer Insulated Wire, Lincoln, R.I.

LEONARD Y. COOPER, Bell Laboratories, Whippany, N. J.

HERBERT H. CORNISH, University of Michigan, Ann Arbor, Mich.

VIGAY COTAIN, Samuel Moore Company, Aurora, Ohio

JOHN F. CURTIS, Todd Shipyards Corp., Seattle, Wash.

PETER J. DAVIS, ERDA, Washington, D. C.

JOSEPH DEASY, General Electric Company, Framingham, Mass.

RICHARD DEBLASIO, Nuclear Regulatory Commission, Washington, D. C.

MIKE DELUCIA, David W. Taylor Naval Ship R&D Center, Annapolis, Md.

M. DUCLOUX, National Bureau of Standards, Washington, D. C.

KEN DUNGAN, Professional Loss Control, Inc., Oak Ridge, Tenn.

JOHN K. DUTTON, Tamaqua Cable Products Corporation, Schuylkill Haven, Pa.

PETER J. DUTTON, Tamaqua Cable Products Corporation, Schuylkill Haven, Pa.

VICTOR H. ESCH, D. C. Fire Department, Potomac, Md.

ART FABRITIIS, Philadelphia Insulation Wire Company, Moorestown, N. J.

EDGAR W. FASIG, Jr., E. I. DuPont deNemours and Company Inc., Wilmington, Del.

RONALD FEIT, Nuclear Regulatory Commission, Washington, D. C.

THEODORE M. FISCHER, Belden Corporation, Genera, Ill.

DON FOTI, Nel-Pia, Farmington, Conn.

RONALD FRALEIGH, Dow Corning Corporation, Midland, Mich.

LOUIS J. FRISCO, Raychem Corporation, Menlo Park, Calif.

GEORGE A. GANT, Dow Corning Corporation, Midland, Mich.

ALFRED GARSHICK, Boston Insulated Wire and Cable Company, Boston, Mass.

WILLIAM E. GIBBS, Foster Grant Company Inc., Leominster, Mass.

ALFRED R. GILBERT, Genral Electric Company, Schenectady, N. Y.

DANIEL J. GILLETT, Uniroyal, Inc., Washington, D. C.

R. A. GUBA, The Okonite Company, Ramsey, N. J.

ERNEST H. HALPERN, David Taylor Naval Ships R&D Center, Annapolis, Md.

STEPHEN B. HAMILTON, General Electric Company, Bridgeport, Conn.

ROGER W. HANDORF, Anaconda/Continental Wire and Cable Corporation, York, Pa.

RUSSELL A. HEMSTREET, Factory Mutual Research Corporation, Norwood, Mass.

WILLIAM R. HERRERA, Southwest Research Institute, San Antonio, Tex.

JOHN HOGAN, Cary Chemicals, Inc., Edison, N. J.

CLAYTON HUGGETT, National Bureau of Standards, Washington, D. C.

CHARLES S. ILARDO, Hooker Research, Grand Island, N. Y.

ARIE ILZETZKI, U.S. Consumer Product Safety Commission, Bethesda, Md.

JOHN D. INGHAM, Jet Propulsion Laboratory, Pasadena, Calif.

JOSEPH JACISIN, Bell Laboratories, Whippany, N. J.

JOHN JEANMONOD, Boston Insulated Wire and Cable, Dorchester, Mass.

HENRY I. JEHAN, Plastoid Corporation, Hamburg, N. J.

ROBIN L. JOHNSON, The Anaconda Company, Marion, Ind.

W. D. JONES, Uniroyal, Inc., Washington, D. C.

RONALD KASPER, Industrial Risk Insurers, Hartford, Conn.

STANLEY KAUFMAN, Bell Telephone Laboratories, Norcross, Ga.

ISRAEL KATZ, Northeastern University, Boston, Mass.

STEVE KEITH, Superior Cable Corporation, Hickory, N. C.

C. J. NOEL KELLY, E. B. Industries, Simsburry, Conn.

JOHN P. KELLY, Rollins Burdick Hunter Company, New York, N. Y.

MICHAEL J. KEOGH, Union Carbide Corporation, Bound Brook, N. J.

WILLIAM H. KING, Jr., U.S. Consumer Product Safety Commission, Washington, D. C.

JACOB B. KLEVAN, Rolf Jensen and Associates, Inc., Annandale, Va.

CHARLES E. KRAMER, Celanese Research Company, Summit, N. J.

ROBERT E. KRAUS, Raychem Corportion, Menlo Park, Calif.

NEIL KRIVANEK, E. I. DuPont de Nemours and Company, Wilmington, Del.

JOSEPH W. LANDERS, The Flamemaster Corporation, Sun Valley, Calif.

DAVID H. LAURIDSEN, Kemper Insurance Companies, Summit, N. J.

M. LAURIENTE, Department of Transportation, Washington, D. C.

R. D. LAWRENCE, E. I. DuPont de Nemours and Company, Wilmington, Del.

DAVID F. LAWSON, Firestone Tire and Rubber, Akron, Ohio

T. H. LING, The Anaconda Co., Marion, Ind.

R. LIEPINS, Research Triangle Institute, Research Triangle Park, N. C.

JONATHAN LIPOWITZ, Dow Corning Corporatio, Midland, Mich.

ANNE LIPSKA, Lawrence Livermore Laboratory, Livermore, Calif.

IRVING LITANT, DOT Transportation Systems Ctr, Cambridge, Mass.

D. R. LUH, E. I. DuPont de Nemours and Company, Wilmington, Del.

JAMES D. MACEWEN, University of California, Dayton, Ohio

LORNE L. MACMONAGLE, General Electric Company, Erie, Pa.

PETER R. MCCLURE, Reichhold Chemicals, Inc., Mansfield, Mass.

ROBERT MCCOY, Yankee Atomic Electric Company, Westboro, Mass.

ROBERT MCGOWAN, Naval Ship Engineering Center, Washington, D. C.

CHARLES R. MCKAY, E. I. DuPont de Nemours and Company, Wilmington, Del.

JOHN TODD MCLANE, David Taylor Naval Ship R&D Center, Annapolis, Md.

HOWARD F. MCRAE, Haveg Industries, Winooski, Vt.

D. P. MACAIONE, U.S. Army Materials & Mechanics Research Center, Watertown, Mass.

STANLEY B. MARTIN, Stanford Research Institute, Menlo Park, Calif.

S. MICHALOWSKI, General Cable Corporation, Union, N. J.

J. M. MEYER, E. I. DuPont de Nemours and Company, Wilmington, Del.

JOHN J. MOLLOY, E. B. Industries, Simsburry, Conn.

JAMES P. MORAN, Aluminum Association, New York, N. Y.

ROBERT A. MURPHY, The Flamemaster Corporation, Sun Valley, Calif.

LARRY D. MUSCHLITZ, TRW Crescent Wire and Cable, Trenton, N. J.

KEN MUSSELMAN, Naval Surface Weapons Center, Dahlgren, Va.

M. E. NICHOLAS, Honeywell, Bloomington, Minn.

MAYNARD G. NOBLE, General Electric Co., Waterford, N. Y.

ROBERT A. PACE, Duke Power Company, Charlotte, N.C.

CUTTER D. PALMER, E. I. DuPont de Nemours and Company, Wilmington, Del.

BALDEOBHAI S. PATEL, The Anaconda Company, Marion, Ind.

VINAY PATEL, Alpha Wire Corporation, Elizabeth, N. J.

ELI M. PEARCE, Polytechnic Institute of New York, Brooklyn, N. Y.

JOSEPH PERKINS, E. I. DuPont de Nemours and Company, Wilmington, Del.

PAT PHILLIPS, ERDA-Nevada Operations, Las Vegas, Nev.

JAN S. PIRRONG, Public Service Electric and Gas, Newark, N. J.

PETER PLIMMER, E. I. DuPont de Nemours and Company, Parkersburg, W. Va.

WILLIAM R. PRINDLE, National Academy of Sciences, Washington, D. C.

GEORGE S. PRISTACH, NYC Transit Authority, Brooklyn, N. Y.

LARRY PTASCHEK, Philadelphia Insulated Wire, Moorestown, N. J.

JOHN O. PUNDERSON, E. I. DuPont de Nemours and Company, Parkersburg, W. Va.

ROBERT RAUFMAN, Western Electric Company, Norcross, Ga.

L. H. ROBINSON, Canada Wire and Cable, Ltd, Toronto, Canada

GUMERSINDO RODRIGUEZ, David Taylor Naval Ship R&D Center, Annapolis, Md.

F. LEE RODKEY, Naval Medical Research Institute, Bethesda, Md.

J. ROSE, Essex Group, Inc., Lafayette, Ind.

SOL RUBINSTEIN, General Cable Research Laboratory, Union, N. J.

DONALD C. SANDERS, FAA-Civil Aeromedical Institute, Oklahoma City, Okla.

ROBERT SAWYER, Nel-Pia, Farmington, Conn.

DAVID SCHNIEDER, Thermo Electric Company, Inc., Salle Brook, N. J.

ROBERT S. SHANE, National Academy of Sciences, Washington, D. C.

BEN SMITH, Naval Surface Weapons Center, Dahlgren, Va.

MASAMI SORIMACHI, Hitachi Cable Ltd., New York, N. Y.

GEORGE SORKIN, Naval Sea Systems Command, Washington, D. C.

CONRAD SPRING, Bell Laboratories, Whippany, N. J.

CHARLES STANTON, ICORE International, Sunnyvale, Calif.

GERHARD STOECKL, Cable Consultants Corporation, Larchmont, N. Y.

DON STONKUS, Ontario Hydro, Toronto, Canada

CLAUDE STRAUB, Naval Ship Engineering Center, Washington, D. C.

STEVEN STREITEL, Alpha Wire Corporation, Elizabeth, N. J.

DAVID TATE, Firestone Tire and Rubber Company, Akron, Ohio

PHILIP A. THOMAS, The Protectowire Company, Hanover, Mass.

JOHN F. TOBIN, Naval Ship Engineering Center, Washington, D. C.

HARVEY P. UTECH, The Fire Independent, Washington, D. C.

JURI VIRKUS, General Cable Corporation, Union, N. J.

C. WASSOUT, Essex Group, Inc., Marion, Ind.

THOMAS E. WATERMAN, IIT Research Institute, Chicago, Ill.

TOM WEIBEL, F.M.C. Corporation, Princeton, N. J.

WALTER G. WELLS, American Iron and Steel Institute, Washington, D. C.

RICHARD E. WIBERG, NIOSH/ALOSH, Morgantown, W. Va.

JAMES WINGER, National Bureau of Standards, Washington, D. C.

JACK A. WINSTEAD, National Academy of Sciences, Washington, D. C.

WILLIAM WOODROW, Raychem Corporation, Menlo Park, Calif.