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NATIONAL RESEARCH COUNCIL OF CANADA DIVISION OF BUILDING RESEARCH

DBR INTERNAL REPORT NO. 502

TOXICITY AND SMOKE ASPECTS OF FOAMED PLASTIC INSULATION An Annotated Bibliography

by K.K. Choi

Checked by: Approved by: L.W. Gold Date: July 1985

Prepared for: Records Purposes. Also submitted to NRC/SPI Joint Co-ordinating Committee.

ABSTRACT

The toxicity and smoke aspects of foamed plastic insulation under fire conditions have been studied by many researchers and numerous papers have been published. This annotated bibliography is the result of an effort to gather and review some of the publications on these subjects.

ANALYZED

INTRODUCTION

The toxicity and smoke aspects of foamed plastic insulation under fire conditions have been studied by many researchers and numerous papers have been published. This annotated bibliography is the result of an effort to gather and review some of the publications on these subjects.

The references are retrieved by a profile search via the CAN/SDI system of CISTI (Canadian Institute for Scientific and Technical Information) and a manual search through the appropriate technical journals. The following is a list of the journals from which the references cited in this bibliography have been located.

	No. of References	Periods Covered
Journal of Cellular Plastics	2	Aug 74 to Dec 77
Journal of Combustion Toxicology	20	Feb 74 to Nov 81
Journal of Consumer Product Flammability	3	Jun 76 to Sep 77
Journal of Fire & Flammability	8	Jul 70 to Oct 79
Journal of Fire Retardant Chemistry	5	Feb 74 to Nov 80
Journal of Fire Sciences	2	Apr 83 to Oct 83
Journal of Thermal Insulation	8	Oct 77 to Apr 81
Fire and Materials	7	Mar 76 to Mar 84
Fire Technology	6	Aug 77 to Aug 81
Modern Plastics	4	Jul 77 to Sep 80

It must be pointed out that pertinent information also appears in conference proceedings, internal reports, research notes, and books. These sources are not used during the compilation of this bibliography because experience shows that data and discussions presented in books tend to be too general in nature; conference papers, etc. are not widely distributed and easily accessible, and are usually re-published in technical journals.

The bibliography is divided into two parts to deal with the toxicity and the smoke aspects of foamed plastic insulation separately. Within each part, the references are listed in chronological order with the most recent publications appearing first. In the annotation, only the results of phenolic, polyisocyanurate, polystyrene and polyurethane insulation materials are noted and commented on. The codes in brackets preceding each reference indicate which of these insulation materials have been included in the study: PH for phenolic, PI for polyisocyanurate, PS for polystyrene and PU for polyurethane.

A wealth of information is presented by the references in this bibliography. In general, there seems to be no definite proof that under fire conditions, foamed plastic insulation presents greater toxicological hazards and smoke problems than conventional organic materials.

A. TOXICITY

(PU)

Purser, D.A. and Grimshaw, P., "The Incapacitative Effects of Exposure to the Thermal Decomposition Products of Polyurethane Foams", <u>Fire and Materials</u>, Vol. 8, pp. 10-16 (March 1984).

The mechanisms of incapacitation resulting from exposures to the thermal decomposition products of flexible and rigid polyurethane foams were studied over a range of different temperatures under pyrolytic or non-flaming oxidative decomposition conditions. When rigid polyurethane foam was oxidized at $600\,^{\circ}\text{C}$, clear atmosphere containing CO and HCN was produced and the sign of toxicity was similar to that produced by HCN alone.

(PS, PU)

Purser, D.A. and Woolley, W.D., "Biological Studies of Combustion Atmospheres", J. of Fire Sciences, Vol. 1, pp. 119-144 (March/April 1983).

The mechanisms of incapacitation resulting from exposures to atmospheres of thermal decomposition products from polymeric materials were studied. The main findings were that the composition and hence the toxicity of the products from individual materials could vary considerably depending upon the different conditions of temperature and degree of oxygenation, however, the basic toxic effects on the animals were relatively simple. For each individual test atmosphere the toxicity was always dominated by either CO, or HCN or irritants. The atmosphere produced by the non-flaming oxidative decomposition of rigid polyurethane foam was clear with high yields of CO and HCN while that of polystyrene was smoky and irritating, and contained small amounts of CO.

(PU)

Zitting, A., Rosenberg, C., Vainiotalo, S. and Savolainen, H., "Toxicity of Polyurethane-derived Oxidative Thermal Decomposition Products", <u>Fire and Materials</u>, Vol. 6, pp. 96-98 (June 1982).

Male wistar rats were exposed to the thermo-oxidative degradation products of a MDI-based polyurethane foam induced at relatively low temperature (410°C) in order to study the chronic toxicity effect at work places where polyurethanes are used. Test data do indicate a toxic hazard associated with the thermal processing and production of polyurethane goods.

(PU)

Michal, J., "Determination of Hydrogen Cyanide in Thermal Degradation Products of Polymeric Materials", <u>Fire and Materials</u>, Vol. 6, pp. 13-15 (March 1982).

This paper describes the use of a spectrophotometric method to investigate the hydrogen cyanide formation in the pyrolytic and thermo-oxidative degradation of commercial, nitrogen-containing polymers such

as polyamides, polyimides and polyurethanes. Results indicate that the amount of HCN generated is temperature dependent. The amount of HCN produced increases quickly at temperatures above 800°C.

(PU)

Lieu, P.J., Magill, J.H. and Alarie, Y.C., "Flammability-Toxicity Ratings of Some Polyphosphazene and Polyurethane Foams", <u>J. of Combustion Toxicology</u>, Vol. 8, pp. 242-259 (November 1981).

The toxicity of the degradation products in air of several polyphosphazenes were tested using mice. Douglas Fir was used as a reference material in these screening tests. The authors proposed a new formula called potential hazard index (PHI) for comparative screening of polymeric materials. Comparison of the potential hazard indices between polyphosphazenes and flexible and rigid polyurethanes shows that the polyphosphazenes are superior in terms of overall hazard ratings.

(PS, PU)

Hilado, C.J. and Huttlinger, P.A., "Toxic Hazards from Common Materials", Fire Technology, Vol. 17, pp. 177-182 (August 1981).

Off-gas toxicity data on materials commonly found in the kitchen are presented to provide a practical perspective on relative toxicity. Materials evaluated included polystyrene foam egg carton and flexible polyurethane foam cushion. The majority of the synthetic plastics and foams which may be present throughout a residence appear to present no greater toxic hazard potential than many food materials, and less toxic hazard potential than wood.

(PH)

Hilado, C.J. and Huttlinger, P.A., "Toxicity of Off-Gases from Phenolic Rigid Foam", J. of Combustion Toxicology, Vol. 2, pp. 121-124 (May 1981).

A reference sample of phenolic rigid foam was evaluated for toxicity of off-gases, using various test conditions in the NASA-USF-PSC toxicity screening test method. Test results shown that the response of this material to the various test conditions is similar to that exhibited by the majority of other materials previously evaluated by this method. That is, animal response times generally decreased with increasing fixed temperature, and with increasing air flow rate under rising temperature conditions. The authors suggest that formaldehyde is one of the toxicants present although the amount of CO produced at 600°C or higher was enough to be lethal by itself.

(PH, PI, PS, PU)

Hilado, C.J. and Huttlinger, P.A., "Toxicity of Off-Gases from Thermal Insulation", J. of Thermal Insulation, Vol. 4, pp. 276-287 (April 1981).

Toxicity test data on the off-gases from various thermal insulation materials are presented in this paper. Under rising temperature

without forced air flow test conditions, phenolic foams exhibited the shortest times to death, while polyisocyanurate, polyurethane and polystyrene foams exhibited the longest times to death. The introduction of air flow significantly reduced time to death, apparently due to a higher degree of oxidation and more rapid delivery of toxicants. The authors conclude that under the particular test conditions, plastic thermal insulations appear to exhibit less toxicity than cellulosic board and cellulose insulation, with polyimide and phenolic foams being the exceptions.

(PH, PI, PS, PU)
Hilado, C.J. and Huttlinger, P.A., "Pyrolysis of Polymeric Materials: III.
Effect of Chemical Structure and Temperature on Carbon Monoxide Evolution",
J. of Fire & Flammability, Vol. 12, pp. 65-71 (January 1981).

Carbon monoxide evolution was determined for samples of polymeric materials under rising and fixed temperature conditions, as well as fixed and varying sample weights. The results show that the yield of CO is a function of chemical composition, temperature, and sample weight. Under rising temperature and fixed sample weight conditions, phenolic exhibited the highest yield of CO among the rigid cellular polymers, but lower than hardwoods such as aspen poplar and yellow birch. The lower CO yields did not necessarily indicate lower toxicity, however, because the principal toxicants of the nitrogen-containing polymers appeared to be compounds other than carbon monoxide.

(PH, PI, PS, PU)
Hilado, C.J. and Huttlinger, P.A., "Relative Flammability and Toxicity of Thermal Insulation", J. of Thermal Insulation, Vol. 4, pp. 217-222 (January 1981).

Relative flammability and relative toxicity data are presented for 30 samples of thermal insulation materials. There appears to be no inherent, necessary compromise between flammability and toxicity in the selection of materials. Cellulosic and plastics insulations appear to represent significantly different combinations of flammability and toxicity hazards, and require different approaches when planning and designing applications. Polyurethane foam appeared to be significantly less toxic and slightly less flammable than wood and other cellulosic materials. Polyisocyanurate foam seemed to be more toxic than polyurethane foam but still less toxic than the cellulosic materials. Polystyrene foam exhibited the longest time to death while phenolic foam showed the second shortest time to death among the group of rigid foams evaluated.

(PU)
Hilado, C.J. and Huttlinger, P.A., "Effect of Fire Retardants on Toxicity of Off-Gases: A Review of Work Done Using the NASA-USF Method", J. of Fire Retardant Chemistry, Vol. 7, pp. 206-209 (November 1980).

Studies on toxicity of off-gases from materials without and with fire retardants, using the NASA-USF method, were reviewed. In the case with polyurethane rigid foam, the use of fire retardant appeared to either be beneficial or have no significant effect under the particular test conditions.

(PH, PI, PS, PU)
Hilado, C.J. and Huttlinger, P.A., "Carbon Monoxide Production From
Overheated Thermal Insulation Materials", J. of Thermal Insulation, Vol. 4,
pp. 87-92 (October 1980).

Carbon monoxide yields were obtained for selected thermal insulation materials. The data are presented and discussed in this paper. Among the rigid foamed plastics, phenolic gave the highest yield of CO under a rising temperature and no air flow test conditions. Polyurethane foams based on propoxylated aromatic amino polyol appeared to produce less CO than polyurethane foams based on propoxylated trimethylolpropane polyol. Under fixed temperatures of 800°C without air flow test conditions, similar results were obtained for the rigid foamed plastics.

(PS)
Hilado, C.J. and Huttlinger, P.A., "Rising vs. Fixed Pyrolysis Temperature in Evaluating Toxicity", Modern Plastics, Vol. 57, pp. 89, 94 (September 1980).

This paper discusses the pros and cons between rising and fixed temperature toxicity test methods. Data obtained by both methods are presented and compared. The authors conclude that the use of the rising-temperature method in evaluating toxicity effects appears to be a reasonably precise means of integrating the toxic effects of gases which are produced over a certain temperature range, with a cost reduction greater than 80% relative to a succession of fixed temperatures. Data show that polystyrene performs better than Douglas Fir in terms of survival times of the test animals in both test methods.

(PI, PU)
Kimmerle, G. and Prager, F.K., "The Relative Toxicity of Pyrolysis Products. Part II. Polyisocyanate Based Foam Materials", J. of Combustion Toxicology, Vol. 7, pp. 54-68 (February 1980).

The acute toxicity of pyrolysis products of isocyanate-based foam materials were compared to those of natural products like wood, cork, wool and cotton. The results obtained from animal experiments using the dynamic test procedure described in DIN Draft 53436 showed that the natural products produce pyrolysis gases of equal, lesser and greater toxicity than the polymeric materials, using the test conditions described in this report. The authors conclude that it is not possible to totally assess the toxicity of combustion products on the basis of chemical formulae or chemical analyses. Animal exposure tests, as

well, are required to better understand the performance of different materials when being pyrolyzed or burned.

(PH, PI, PS, PU)
Hilado, C.J. "Carbon Monoxide as the Principal Toxicant in the Pyrolysis Gases from Materials", J. of Combustion Toxicology, Vol. 6, pp. 177-184 (August 1979).

Total concentration-time exposure to carbon monoxide was estimated for toxicity screening tests on 93 materials, including polyurethane, phenolic, polyisocyanurate and polystyrene foams, using death-product (DP) values based on the CO analyses at the end of the tests. On the basis of the calculated DP values, carbon monoxide appears to have been the sole toxicant or principal toxicant in the gases from the majority of materials evaluated. Among the rigid cellular polymers evaluated, phenolic is the only one that shows a DP value above the critical one, indicating that for other foam materials, toxicants other than CO are responsible for the toxicity performance.

(PH, PI, PS, PU)
Hilado, C.J. and Casey, C.J., "Pyrolysis of Polymeric Materials: I. Effect of Chemical Structure, Temperature, Heating Rate, and Air Flow on Char Yield and Toxicity", J. of Fire & Flammability, Vol. 10, pp. 140-167 (April 1979).

Various polymeric materials were evaluated at different temperatures, heating rates, and air flow rates for thermophysical and toxicological responses using thermogravimetric and USF toxicity screening test methods. The materials included polyisocyanurate, polyurethane, polystyrene and phenolic foams. For polymers containing only carbon, hydrogen and oxygen, test results indicate that toxicity is strongly related to CO concentration, and that increasing char yield from 0 to 20% decreases toxicity by decreasing CO concentration. For polymers containing nitrogen, the increasing toxicity and decreasing CO concentration as char yield increases above 20% indicate that toxicants other than CO are playing an increasingly significant role with increasing char yield.

(PS)
Hilado, C.J. and Brauer, D.P., "How Test Conditions and Criteria Affect
Pyrolysis-Gas Toxicity Findings", Modern Plastics, Vol. 56, pp. 62-65 (March 1979).

This paper compares the toxicity performance of various plastics and nonplastics materials under different test conditions. Data indicate that the relative toxicity of pyrolysis gases varies considerably, depending on the temperature and air flow used, and on whether mortality, time to death, or carbon monoxide concentration is the criterion of toxicity. Under a rising temperature condition, polystyrene gave the longest time to death among the materials tested, however, under other conditions, it can also appear to be less toxic, or as toxic as Douglas Fir.

(PU)

Hilado, C.J. and Brauer, D.P., "The Effect of Fire Retardants on Combustibility and Toxicity", <u>J. of Fire Retardant Chemistry</u>, Vol. 6, pp. 20-26 (February 1979).

The effects of fire retardants on ignitability, flash-fire propensity, smoke and toxicity of four polyurethane rigid foams were studied. The results showed that the use of fire retardants to increase flame resistance appeared to be beneficial or to have no effect on these characteristics.

(PH. PI)

Hilado, C.J., Huttlinger, N.V. and Brauer, D.P., "Toxicity of Pyrolysis Gases from Phenolic and Isocyanurate Rigid Foams", J. of Combustion Toxicology, Vol. 5, pp. 391-399 (November 1978).

Special reference samples of phenolic and isocyanurate rigid foams were evaluated for toxicity of pyrolysis gases, using 6 different test conditions of the USF toxicity screening test methods. Under rising temperature conditions, phenolic foam appeared to be consistently more toxic than the isocyanurate foam. CO level appears to be the factor, which is twice as high from the phenolic foam. The temperatures corresponding to the times to death indicate that the toxicants were evolved below 500°C for phenolic and below 640°C for isocyanurate. These are in agreement with that of the University of Pittsburgh (UP) data. At a fixed temperature of 800°C, there appeared to be no difference in toxicity between the phenolic and isocyanurate foams, although the former tended to produce more carbon monoxide.

(PI, PS, PU)

Hilado, C.J., Cumming, H.J. and Machado, A.M., "Relative Toxicity of Pyrolysis Gases from Materials: Specific Toxicants and Special Studies", $Fire\ and\ Materials$, Vol. 2, pp. 141-153 (October 1978).

Various aspects of pyrolysis gas toxicity studies at the USF are discussed, and animal response data as well as reference time—concentration curves for individual gaseous toxicants are presented. The authors suggest that the animal response data can be used to establish patterns which would help identify specific toxicants by their mode of action while time—concentration curves can be used to permit deduction of the importance of individual toxicants in complex mixtures of toxic gases. The authors further suggest that these techniques can be used to identify causes and mechanisms of toxicity without significant additional cost. Data presented on rigid cellular polymers include polyurethanes, polyisocyanurates and polystyrenes.

(PH, PI, PS, PU)

Hilado, C.J. and Brauer, D.P., "Toxicity of Pyrolysis Gases from Thermal Insulation Materials", J. of Thermal Insulation, Vol. 2, pp. 90-101 (October 1978).

This paper presents the toxicity test data on various thermal insulation materials, and discusses the effect of test parameters and the relationship between char yield and toxicity. With the exception of polyimide and phenolic rigid foams, commercial rigid cellular plastic insulations appear to exhibit less toxicity than cellulosic board and cellulose insulation under the particular test conditions. The toxicity of the gases evolved seems to increase with increasing char yield for most thermal insulation material.

(PI, PS, PU)

Hilado, C.J. and Machado, A.M., "Char Yield and Toxicity of Pyrolysis Gases from Materials", J. of Fire & Flammability, Vol. 9, pp. 367-376 (July 1978).

Comparison of the char yield at the time to death observed in Swiss Webster male mice exposed to the pyrolysis gases from various polymeric materials indicates that increased char yield is not necessarily associated with reduced toxicity. Among the rigid cellular polymers, the relative toxicity of the pyrolysis gases seemed to generally increase with increasing char yield except for polystyrene which melted instead.

(PH, PI, PS)

Hilado, C.J. and Huttlinger, N.V., "Toxicity of Pyrolysis Gases from Phenolic, Isocyanurate and Polystyrene Rigid Foam Insulation", J. of Thermal Insulation, Vol. 2, pp. 40-47 (July 1978).

Samples of phenolic, isocyanurate, and polystyrene rigid foam insulation were evaluated for toxicity of pyrolysis gases, using four different test conditions of the toxicity screening test method developed at the University of San Francisco. The test conditions were 200 to 800°C rising temperature and 800°C fixed temperature, each without forced air flow and with 1 L/min air flow. On the average over these four particular test conditions, phenolic foam appeared to exhibit the greatest toxicity and polystyrene foam appeared to exhibit the least toxicity.

(PH, PI, PS, PU)

Anderson, R.S., Stock, M.F. and Alarie, Y.C., "Toxicologic Evaluation of Thermal Decomposition Products of Synthetic Cellular Materials. Part I", J. of Combustion Toxicology, Vol. 5, pp. 111-129 (May 1978).

The thermal decomposition products from a series of synthetic polymeric cellular materials and Douglas Fir were investigated. Using sensory irritation (RD_{50}) and stress index measurements, the authors show that it is possible to obtain comparisons of the potency of the thermal decomposition products. The approach used can also yield information on the duration of exposure-concentration-level of response relationships which is needed for evaluating toxicity of thermal decomposition products of materials. Test data are presented both in tabulated and graphical forms.

(PI, PS, PU)

Hilado, C.J. and Machado, A.M., "Toxicity of Pyrolysis Gases from Some Cellular Polymers", J. of Combustion Toxicology, Vol. 5, pp. 162-181 (May 1978).

Various samples of cellular polymers were evaluated for toxicity of pyrolysis gases, using the USF toxicity screening test method. The cellular polymers exhibited varying levels of toxicity under these test conditions. Among the rigid foams evaluated, times to death were shortest with polyimide and polyisocyanurate, and longest with polystyrene. CO did not appear to be the sole toxicant in the polyisocyanurate and some polyurethane rigid foams, and increased char yield was not necessarily associated with reduced toxicity if CO is not the principal toxicant.

(PU)

Hilado, C.J., Schneider, J.E. and Murphy, R.M., "Effect of Fire Retardant on Relative Toxicity of Pyrolysis Gases from Polyurethane Foams", J. of Fire Retardant Chemistry, Vol. 5, pp. 83-85 (May 1978).

The relative toxicity of pyrolysis gases of polyurethane foams with different concentrations of fire retardant was studied, using the USF toxicity screening test method. The results show that once a certain level of ignition resistance is obtained by the incorporation of fire retardant, additional fire retardant seems to have no significant effect on pyrolysis gas toxicity.

(PI, PS)

Hilado, C.J., Cumming, H.J. and Casey, C.J., "Toxicity of Pyrolysis Gases from Natural and Synthetic Materials", Fire Technology, Vol. 14, pp. 136-146 (May 1978).

The authors present toxicity data on various natural and synthetic materials under simulated fire conditions, provide comparisons between materials, and discuss the significance of the data and the impact of public acceptance. Relatively few synthetic materials appear to be more toxic than the commonly accepted natural materials, such as wood, cotton, wool and silk under the particular test conditions. Among the synthetic polymers, polystyrene and polyisocyanurate rigid foam appeared to exhibit the longest time to incapacitation.

(PI, PS, PU)

Hilado, C.J. and Cumming, H.J., "Relative Toxicity of Pyrolysis Gases from Materials: Effects of Chemical Composition and Test Conditions", Fire and Materials, Vol. 2, pp. 68-79 (April 1978).

Relative toxicity test data on 270 materials, including polyurethane, polyisocyanurate and polystyrene foams are presented, based on test procedures developed at USF. The materials evaluated under this test condition (rising temperature, no forced air flow) exhibited a broad range of relative toxicity performance. Changing to a fixed temperature program, and changing to a fixed air flow situation

generally resulted in shorter times to incapacitation and times to death. The relative rankings of materials tended to remain the same in spite of changes in test conditions and in test methods although some significant reversals in ranking were also observed.

(PI, PS, PU)

Hilado, C.J., Cumming, H.J. and Casey, C.J., "Relative Toxicity of Materials in Fire Situations", Modern Plastics, Vol. 55, pp. 92-96 (April 1978).

This article presents some of the relative toxicity data on polymers by generic type resulting from work carried out at the University of San Francisco. Data on wood and cellulose board are also included for comparison purposes. Among the findings of interest is that polystyrene and polyisocyanurate rigid foams appeared to exhibit the longest times to incapacitation of all materials tested. The authors suggest that if the natural cellulosic materials (wood and cotton) are considered acceptable in a residential environment, there appear to be relatively few polymeric materials that could be considered significantly more toxic than these baseline materials.

(PI, PS, PU)

Hilado, C.J., Cumming, H.J. and Schneider, J.E., "Relative Toxicity of Pyrolysis Gases from Some Rigid Foams Used as Thermal Insulation", J. of Thermal Insulation, Vol. 1, pp. 215-220 (January 1978).

Various samples of rigid foams used as thermal insulation were evaluated for toxicity of pyrolysis gases, using the USF toxicity screening test method. The samples included polyurethane, polyisocyanurate and polystyrene. The toxicity of pyrolysis gases from polyurethane rigid foams seem to depend on foam composition. The polyisocyanurate foams appear to be comparable with the least toxic polyurethanes while polystyrene foams exhibit the longest time to death. The rising temperature and fixed temperature methods produced the same ranking order based on time to death.

(PU)
Hilado, C.J., Cumming, H.J. and Solis, A.N., "Relative Toxicity and Flash Fire Propensity of the Pyrolysis Gases from Polyurethane Foams", J. of Cellular Plastics, Vol. 13, pp. 408-415 (Nov/Dec 1977).

Samples of rigid and flexible polyurethane foams were evaluated for pyrolysis gases toxicity and flash fire propensity by test methods developed at the University of San Francisco. The wide range in toxicity performance among the samples emphasizes the inadvisability of considering any level of performance as representative. The effect of fire retardants on relative toxicity was either not significant or beneficial under these particular test conditions. Unusual toxic effects were observed under test conditions so specific that doubts are raised as to whether they are likely to be encountered in real fires and whether any set of test conditions can permit identification of all possible unusual toxicants.

(PI, PU)

Hartung, R., Ball, G.L., Boettner, E.A., Rosenbaum, R. and Hollingsworth, Z.R., "The Performance of Rats on a Rotarod During Exposure to Combustion Products of Rigid Polyurethane Foams and Wood", J. of Combustion Toxicology, Vol. 4, pp. 506-521 (November 1977).

This paper describes the apparatus and procedure of a rotarod method developed to test the motor performance of rats exposed to thermal degradation products. Results are reported for nonflaming decomposition products from polyurethane, polyisocyanurate foams and Douglas Fir in terms of time-to-incapacitation. Test data indicate that the test is capable of detecting statistically significant differences in the level of functional impairment produced by different samples of foams and wood. One of the foam samples produced very significantly longer time-to-incapacitation and another produced marginally longer time-to-incapacitation than Douglas Fir. Other samples indicate statistically insignificant difference in performance when compared to the wood sample.

(PS)

Hilado, C.J. and Cumming, H.J., "The Effect of Test Conditions on the Relative Toxicity of the Pyrolysis Products from Some Plastics", Fire Technology, Vol. 13, pp. 325-328, 338 (November 1977).

The authors discuss the differing results obtained from various test methods used to determine the toxiticy of pyrolysis products. Polystyrene was among the materials investigated. The relative toxicity rankings of the materials tested were highly dependent on the test conditions used, and on the choice of incapacitation or death as the criterion of toxicity.

(PI, PU)

Hilado, C.J. and Cumming, H.J. "Fire Safety Aspects of Thermal Insulation", J. of Thermal Insulation, Vol. 1, pp. 116-128 (October 1977)

This paper discusses some of the fire safety aspects of thermal insulation. One section is devoted to fire toxicity considerations in which relative toxicity data on some construction and thermal insulation materials are presented. Under the particular test conditions used, polyurethane and polyisocyanurate rigid foams produced pyrolysis gases no more toxic than the normally accepted construction materials.

(PI, PS, PU)

Hilado, C.J. and Cumming, H.J., "A Compilation of Relative Toxicity Data", J. of Consumer Product Flammability, Vol. 4, pp. 244-266 (September 1977).

Relative toxicity data on 270 materials evaluated at the University of San Francisco (USF) are presented, using 10 different sets of test conditions. Rigid and flexible polyurethane foam, polyisocyanurate foam, and polystyrene were among the materials evaluated. These materials did not appear to be more toxic in terms of time-to-death or

time-to-incapacitation when compared with wood on a generic basis although a broad range of relative toxicity performance was observed. Polystyrene is one of the polymers that gave the longest time to incapacitation.

(PI, PS, PU)
Hilado, C.J., "Screening Materials for Relative Toxicity in Fire Situations", Modern Plastics, Vol. 54, pp. 64-69 (July 1977).

Results of screening tests of materials for relative toxicity under specific sets of conditions are presented. Variation in the materials, lab animals, and in the test permit identification of major rather than minor differences among materials. Correlation with relative performance in real fire situations is based on a limited number of comparisons. Polyurethane, polyisocyanurate and polystyrene foams were among the materials evaluated. Polyurethane and polyisocyanurate rigid foams show an average toxicity performance while polystyrene shows one of the best toxicity performances in terms of time-to-death for the test animals.

(PU)
Hilado, C.J. and Schneider, J.E., "Toxicity Studies of a Polyurethane Rigid Foam", J. of Combustion Toxicology, Vol. 4, pp. 79-86 (February 1977).

Relative toxicity tests were performed on a polyurethane rigid foam containing a trimethylolpropane-based polyol and an organophosphate flame retardant, a type of combination reported to be unusually toxic. No unusual toxicity was observed with either gradual or rapid pyrolysis to 800°C in the absence of air flow. Convulsions and seizures of test animals were observed when the material was essentially flash pyrolyzed at 800°C in the presence of air flow. These observations are similar to those previously reported, and the toxicity appeared unusual because of the dramatic effect rather than the low sample weights required to produce death.

(PU)
Hilado, C.J. and Slattengren, C.L., "Relative Toxicity of Pyrolysis Products of Some Polyurethane and Polychloroprene Foams", J. of Combustion
Toxicology, Vol. 4, pp. 21-31 (February 1977).

Results of the USF toxicity screening tests on some polyurethane and polychloroprene flexible foams are presented. With a rising temperature test condition, the more toxic materials are associated with the generation of toxicants at lower temperatures. Comparisons indicate that polyurethane foams without fire retardant are more toxic than the corresponding foams with fire retardant, and polychloroprene foams are least toxic.

(PS, PU)

Hilado, C.J., "Relative Toxicity of Products of Pyrolysis and Combustion of Polymeric Materials Using Various Test Conditions", J. of Consumer Product Flammability, Vol. 3, pp. 193-217 (September 1976).

Relative toxicity data are presented on a wide variety of polymeric materials, obtained using 14 different test methods, with 11 based on pyrolysis and 3 based on flaming combustion. Rigid and flexible polyurethane foams, and polystyrene were among the materials evaluated. The author concludes that the test results are sensitive to variables such as exposure mode, temperature, air flow and dilution, concentration of material and animal species, and suggests that times to incapacitation and to death would provide a more suitable basis for relative toxicity ranking than percent mortality alone.

(PU)

Keller, J.G., Herrera, W.R. and Johnston, B.E., "An Investigation of Potential Inhalation Toxicity of Smoke from Rigid Polyurethane Foams and Polyester Fabrics Containing Antiblaze 19 Flame Retardant Additive", J. of Combustion Toxicology, Vol. 3, pp. 296-304 (August 1976).

The previously reported abnormal neurological effects and increased toxicity for the nonflaming decomposition products of certain trimethylolpropane—based rigid polyurethane foams containing flame retardant additives were confirmed by the authors by animal exposure experiments. In similar experiments with rigid polyurethane foams and polyester fabric samples containing a cyclic phosphonate derivative of trimethylolpropane, these effects were not observed. The authors propose an explanation based on the stability of the cyclic phosphonate flame retardant additive.

(PU)

Hilado, C.J. and Saxton, G.L., "Relative Toxicity of Pyrolysis Products of Some Cellular Polymers", J. of Combustion Toxicology, Vol. 3, pp. 259-269 (August 1976).

Twelve samples of cellular polymers including three rigid polyurethane foams with and without fire retardants, were evaluated in the course of developing the USF toxicity screening test method. Test data show that times to incapacitation were between 8 and 11 min, and were not significantly affected by fire retardant. Times to death averaged between 9 and 15 min, and were significantly reduced by the incorporation of chlorinated butylene oxide-based polyol. On the basis of these results, relative toxicity appears to be increased by the incorporation of one fire retardant and not significantly affected by the addition of another.

(PS, PU)

Hilado, C.J. and Miller, C.M., "The Effect of Changes in the USF/NASA Toxicity Screening Test Method on Data from Some Cellular Polymers", J. of Combustion Toxicology, Vol. 3, pp. 237-257 (August 1976).

Relative toxicity rankings can be markedly affected by changes in test variables. The effect of these changes on data from some cellular polymers is addressed in this paper, in terms of comparison with each other and in comparison with other materials. The foam materials tested include rigid polyurethane foam with fire retardant and polystyrene foam.

(PU)
Hilado, C.J. and LaBossiere, L.A., "Evaluation of Some Commercial Materials
Using the USF/NASA Fire Toxicity Screening Test Method", J. of Consumer
Product Flammability, Vol. 3, pp. 141-149 (June 1976).

Twenty samples of commercial materials were evaluated, using the USF/NASA fire toxicity screening test method. Test results and estimates of reproducibility are presented. Under the conditions of test, wool appears to be the most toxic, followed by cotton, polyester, neoprene, aromatic polyamide, flexible polyurethane without flame retardant and flexible polyurethane with flame retardant, in order of decreasing toxicity.

(PU)
Hilado, C.J., "Relative Toxicity of Pyrolysis Products of Some Foams and Fabrics", J. of Combustion Toxicology, Vol. 3, pp. 32-60 (February 1976).

This paper describes the development of the University of San Francisco toxicity screening test method. A limited number of flexible polyurethane foams and fabrics were evaluated in the course of developing the test procedure. The principal variable studied, heating rate, did not affect the relative ranking of the material tested. The data obtained show that modification of conventional flexible polyurethane foams with flame retardants seems to consistently reduce toxicity under pyrolysis conditions.

(PU)
Alarie, Y.C., Wilson, E., Civic, T., Magill, J.H., Funt, J.M., Barrow, C. and Frohliger, J., "Sensory Irritation Evoked by Polyurethane Decomposition Products", J. of Combustion Toxicology, Vol. 2, pp. 139-150 (May 1975).

Upper respiratory tract irritation from the decomposition products of flexible and rigid polyurethane foams with and without flame retardants was evaluated by animal exposure experiments. The flexible foams were found to be more highly irritating than the rigid foams. This was due to the incomplete combustion of the rigid foams and more rapid release of decomposition products from the flexible foams. The addition of flame retardants to the foams did not appreciably alter their thermostability or change the degree of sensory irritation from the decomposition products.

(PU)

Woolley, W.D., "The Production of Free Tolylene Diisocyanate (TDI) from the Thermal Decomposition of Flexible Polyurethane Foams", J. of Combustion Toxicology, Vol. 1, pp. 259-267 (November 1974).

When involved in fires flexible polyurethane foams may release tolylene diisocyanate (TDI) which is known to be a highly toxic material. This paper describes the studies of production of free TDI during the thermal decomposition of flexible polyurethane foams between 200 and 900°C. Data indicate that TDI is formed at low temperatures of 250 to 300°C, but is rapidly destroyed at temperatures above 400°C and completely destroyed at temperatures above 700°C.

(PS, PU)

Hofmann, H.T. and Sand, H., "Further Investigations into the Relative Toxicity of Decomposition Products Given Off from Smouldering Plastics", J. of Combustion Toxicology, Vol. 1, pp. 250-257 (November 1974).

This paper presents and discusses toxicity data of decomposition products given off from smouldering plastics. Materials evaluated include polystyrene and polyurethane rigid foams. Depending on the formulations, and the temperatures of exposure, polyurethane gives off degradation products of varying toxicity which are, on the whole, not more toxic than those of nitrogeneous natural materials such as leather or felt. The decomposition products of polystyrene foam were distinctly less toxic than natural materials such as pinewood, rubber, wool, leather and felt when tested at 400°C and 500°C. The authors conclude that under fire conditions, plastics do not represent any greater toxicological hazard than conventional organic materials.

(PS)
Hofmann, H.T. and Oettel, H., "Relative Toxicity of Thermal Decomposition Products of Expanded Polystyrene", J. of Combustion Toxicology, Vol. 1, pp.236-249 (November 1974).

This paper describes the animal experiments for determining the toxic effect of thermal decomposition products of expanded polystyrene, with particular attention given to CO poisoning. The authors conclude that in the event of a fire, expanded polystyrene involves less toxic hazard than conventional building materials and natural products.

(PI, PU)

Ashida, K., Yamauchi, F., Katoh, M. and Harada, T., "HCN Generation from Urethane and Isocyanurate Foams", J. of Cellular Plastics, Vol. 10, pp. 181-185 (July/August 1974).

The relationships between the amount of HCN generated and the chemical structures of urethane and isocyanurate foams in pyrolysis or combustion were investigated. The maximum amount of HCN was formed at approximately 500°C and was proportional to the nitrogen content of the foams. HCN generation was lower in TDI-based foams than in polymeric isocyanate-based foams, and extremely low in a nitrogen atmosphere.

(PII)

Kishitaui, K. and Nakamura, K., "Toxicities of Combustion Products", J. of Combustion Toxicology, Vol. 1, pp. 104-123 (May 1974).

The toxicities of combustion products from a number of building materials were investigated through two kinds of animal tests using mice. In the first method, the material was heated in a quartz-glass tube maintained at a constant temperature, while in the second, the surface of the material was heated by radiation and a pilot flame of propane gas. Test results show that the toxicity of the combustion product of a material differs greatly depending on its type and the temperature at which it is heated. Nitrogen-containing materials such as polyurethane rigid foam produced the largest amount of HCN at 500°C under the test conditions, and although smoke concentrations were very high, there were cases of mice surviving while conversely, mice died in tests with cement-excelsion board in which smoke concentrations were relatively low. This indicates that the biological effects of smoke are not very great and practically all toxicity effects are determined by the gases in the smoke.

(PI, PS, PU)

Kimmerle, M.G., "Aspects and Methodology for the Evaluation of Toxicological Parameters During Fire Exposure", <u>J. of Combustion Toxicology</u>, Vol. 1, pp. 4-51 (February 1974).

The paper discusses the various toxicological aspects of the major factors responsible for the hazards in a fire and presents some data on the toxicological studies of polymeric materials and natural materials, which include polyurethane, polyisocyanurate and polystyrene foams. With polyurethane and polyisocyanurate foams, most of the animal mortalities can be related to the combined action of CO and HCN, and these materials show a much higher critical temperature of mortality indication than spruce—wood and cork.

(PU)
Sumi, K. and Tsuchiya, Y., "Combustion Products of Polymeric Materials
Containing Nitrogen in their Chemical Structure", J. of Fire & Flammability,
Vol. 4, pp. 15-22 (January 1973).

Five materials (including rigid urethane foam) that contain nitrogen were burned in a flask at 800°C and the amount of HCN, CO and ${\rm CO}_2$ produced were quantitatively analyzed by gas chromatography. The harmful effects of these products to the resulting atmosphere were then evaluated. The results vividly illustrate the potential danger of HCN to a fire environment when materials containing nitrogen are involved in fire.

(PH)
Crowley, D.P., Brash, M.P., Burrell, B.W., Tempesta, F.L. and Niehaus, F.,
"Test Method for the Analysis of Toxic Products from Burning Materials Phenolic Foam", Fire Technology, Vol. 8, pp. 228-236 (August 1972).

The authors maintain that conventional laboratory techniques for pyrolyzing small samples of organic materials will not yield realistic data regarding the toxicity of products released by them during a fire and describe a test method they consider better suited to the purpose. Analysis of the gases evolved from a phenolic foam while tested in the unique fire simulation facility revealed that the following toxic products were produced in small amounts - CO, HF, HCl, HCN and phenol. A method of extending these results to actual field situations, based on mass loss rates of the foam measured in the fire simulation facility, is also presented.

(PU)
Autian, J., "Toxicologic Aspects of Flammability and Combustion of Polymeric Materials", J. of Fire & Flammability, Vol. 12, pp. 239-268 (July 1970).

This article looks at the toxicity problems which may result from the burning or heating of manmade polymeric materials. An appendix is also included to introduce readers to the subject of toxicology. The toxicity results from thermodegradation products of polyurethane foam are briefly discussed.

B. SMOKE

(PI, PU)

Imai, Y., Inukai, T. and Tamashima, M., "Study on Combustibility of Urethane-Modified Polyisocyanurate Foam", J. of Fire Sciences, Vol. 1, pp. 349-361 (September/October 1983).

The combustion behaviour of urethane-modified polyisocyanurate foams and polyurethane foams was compared using specially designed test apparatuses. Smoke generation became maximum at about 600°C for polyisocyanurate foams and at about 500°C for polyurethane foams. The use of high functionality isocyanurate, secondary polyols, low molecular weight polyols or amine catalyst brought much more smoke generation; however, polyisocyanurate foams showed less smoke as compared with polyurethane foams.

(PI, PU)

Chambers, J., Jiricny, J. and Reese, C.B., "The Thermal Decomposition of Polyurethanes and Polyisocyanurates", Fire and Materials, Vol. 5, pp. 133-141 (December 1981).

The thermal decomposition of a number of TDI and MDI-based biscarbamates (model compounds for polyurethane foams) between 200°C and 1000°C was studied in an attempt to understand the chemical changes that are responsible for the generation of smoke and toxic gases during the combustion of these plastics.

(PH, PI, PS, PU)

Hilado, C.J., Murphy, R.M. and Huttlinger, P.A., "Smoke from Thermal Insulation Materials", <u>Fire Technology</u>, Vol. 16, pp. 273-286 (November 1980).

The smoke-producing characteristics of various materials are discussed with particular attention to thermal insulation. The different methods of measuring smoke density are described, and selected data are presented. The authors conclude that the evaluation of the smoke-producing characteristics of thermal insulation materials requires evaluation of each particular product and application in order to select appropriate tests and obtain realistic comparisons between materials. The authors also suggest that some thermal insulation materials can be engineered to provide both greater thermal insulating effectiveness and reduced smoke hazard.

(PH, PS, PU)

Hilado, C.J. and Murphy, R.M., "The Measurement of Smoke from Thermal Insulation", J. of Thermal Insulation, Vol. 3, pp. 272-280 (April 1980).

The smoke-producing characteristics of various materials were evaluated using the Arapahoe, NBS, ASTM, and OSU methods. The different methods are described, and selected data are presented and discussed. The authors conclude that the evaluation of smoke-producing characteristics of thermal insulation materials requires evaluation of each particular

product and application in order to obtain realistic comparisons between materials.

(PI, PU)

Herrington, R.M., "The Rate of Heat, Smoke and Toxic Gases Release from Polyurethane Foams", J. of Fire & Flammability, Vol. 10, pp. 308-325 (October 1979).

The release rates of heat, smoke, CO, CO₂, NO_x, HCN, HBr, O₂ and organic compounds of polyurethane and polyisocyanurate foam samples were monitored in an OSU Release Rate Apparatus. All of the foams tested released measurable concentrations of the monitored combustion products.

(PU)

Bonsignore, P.U. and Levendusky, T.L., "Alumina Trihydrate as a Flame Retardant and Smoke Suppressive Filler in Rigid High Density Polyurethane Foams, J. of Fire & Flammability, Vol. 8, pp. 95-113 (January 1977).

The purpose of this study was to examine the effectiveness of hydrated alumina as a low cost flame retardant and smoke suppressive filler for a polyurethane foam system. Results show that the filler can be used successfully, however, techniques and equipment will need to be developed to handle the relatively high viscosities of hydrate dispersions in polyol components. The use of viscosity reducer such as dimethyl methylphosphonate is beneficial but increases the amount of smoke generated.

(PI, PS, PU)

Brown, J.R. and Dunn, P., "Fire Hazards of Organic Materials - Small Scale Assessment of Flammability and Smoke Generation", <u>Fire and Materials</u>, Vol. 1, pp. 2-8 (March 1976).

The flammability and smoke generation of a number of organic materials used in ships, including polyurethane, polyisocyanurate and polystyrene foams were evaluated by limiting oxygen index method and photometric method respectively. Test data are presented and discussed. The most significant aspect of the development of smoke from the combustion of expanded polymeric materials is that the maximum smoke density occurs in a short time. Fire-retarded polyurethanes generate a substantial amount of smoke that is influenced by the types of fire retardants used while polyisocyanurate generates relatively little smoke and at a slow rate.

(PS)

Robertson, A.F., "Two Smoke Test Methods - A Comparison of Data", Fire Technology, Vol. 10, pp. 282-286 (November 1974).

An investigation was conducted to determine if a correlation exists between two smoke test methods, viz., the NBS Smoke Density Chamber and the FRS Smoke Accumulation Room. Eight materials were tested for their

smoke-producing characteristics by the two different methods, with polystyrene foam being one of the samples. The results show that for most of the materials studied, there were general agreement in photometric measurements of smoke production under both methods. One of the exceptions is polystyrene foam. The FRS results are much lower than those of the NBS measurements. The difference is attributed to the melting nature of polystyrene and the different specimen restraining procedures between the two methods.

(PS, PU)
Lindstrom, R.S., Sidman, K.R., Sheth, S.G. and Howarth, J.T., "Effects of Flame and Smoke Retardant Additives in Polymer Systems", J. of Fire Retardant Chemistry, Vol. 1, pp. 152-169 (August 1974).

The paper discusses the basics of flame retardancy and the major effects that flame retardant systems can have on polymer compounds. A section is devoted to the discussion on flame retardancy of polystyrene and polyurethane foams. The use of coating and filler as means of providing flame retardancy is suggested by the authors. The need to develop flame retardants that will also meet the criteria of smoke and toxic gas generation is also addressed.

(PU)
Birky, M.M., Einhorn, I.N., Seader, J.D., Kanakia, M.D. and Chien, W.P.,
"The Effects of Fire Retardants on the Combustion of Rigid-Urethane Foams",
J. of Fire Retardant Chemistry, Vol. 1, pp. 31-45 (February 1974).

A study was undertaken to determine the parameters which govern the smoke emission characteristics of rigid-urethane foams. The flammability characteristics of a rigid-urethane foam with different concentrations of three different fire retardants were evaluated using small-scale tests. Performance of the retarded polymer from a smoke hazard potential as determined from optical attenuation measurements was generally worse than the unretarded foam. There is some indication, however, that the smoke generation goes through a maximum as the retardant is increased.

(PI, PS, PU)
Tsuchiya, Y. and Sumi, K., "Smoke-Producing Characteristics of Materials",
J. of Fire & Flammability, Vol. 5, pp. 64-75 (January 1974).

The various methods for the determination of the smoke-producing characteristics of materials are critically reviewed. The authors point out that existing tests do not represent the wide range of conditions found in real fires for which the rate of smoke production is governed by the rate of combustion and smoke generation coefficient. A new method is described for determining smoke generation coefficient that is suitable for investigating smoke-producing characteristics of materials under varied conditions of temperature and $\mathbf{0}_2$ concentration. Experimental results indicate that the smoke generation coefficient of wood decreases with increasing temperature and decreasing oxygen in the

atmosphere while the trend is reversed for rigid polyurethane, polystyrene and polyisocyanurate foams.

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Abbreviations

ASTM	American Society for Testing and Materials
CO	Carbon Monoxide
CO	Carbon Dioxide
DIŃ	Deutsche Industrienorm
FRS	Fire Research Station
HBr	Hydrogen Bromide
HC1	Hydrogen Chloride
HCN	Hydrogen Cyanide
HF	Hydrogen Fluoride
MDI	Methylene Diisocyanate
NASA	National Aeronautical and Space Administration
NBS	National Bureau of Standards
NO _x	Oxides of Nitrogen
o ₂ * osu	Oxygen
໐ຣັນ	Ohio State University
PSC	Product Safety Corporation
TDI	Toluene Diisocyanate
UP	University of Pittsburgh
USF	University of San Francisco