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November 1986

Literature Review of Pyrolysis and Combustion Products of Selected Utility Materials

Prepared by
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Kansas City, Missouri

REPORT SUMMARY

SUBJECTS: T&D· Substations / Hazardous/toxic substances

TOPICS: Chemical analysis; Combustion products; Construction materials; Toxicology—hazards; Pyrolysis

AUDIENCE: Environmental managers / Distribution engineers

Literature Review of Pyrolysis and Combustion Products of Selected Utility Materials

This information on the thermal-combustion products of utility fabrication and construction materials can help utilities evaluate potential hazards of equipment and materials in fire situations Grouped by chemical composition, the more toxic degradation products are summarized in the report. However, relative abundance in the utility environment is not taken into account

BACKGROUND

Previous EPRI report EL-4503 presents a literature review of the pyrolysis and combustion products of polychlorinated biphenyl (PCB) substitutes EPRI extended that work to include thermal-degradation products of many utility construction materials The expanded literature search provides background for laboratory work currently under way under the same research project

OBJECTIVES

- To search the literature for thermal-degradation products of utility materials.
- To provide background information for selecting materials to be given priority in laboratory work.

APPROACH

Investigators reviewed the published literature—primarily from 1967 to the present—on pyrolysis (heating in nitrogen, helium, or other inert atmosphere), combustion (heating in air or oxygen), or other thermal degradation of 26 utility materials. These materials, including polymers, rubbers, adhesives, films, fluids, coatings, and miscellaneous materials, are used in electrical insulation or construction, such as gaskets and wood preservation The project team grouped the materials according to their chemical composition—whether they contained chlorine, fluorine, nitrogen, and sulfur or only carbon, hydrogen, and/or oxygen

RESULTS

Pentachlorophenol and its sodium salt produce polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans Several polycyclic aromatic hydrocarbons (PAHs), many of which are known carcinogens are produced from combustion or pyrolysis of polyethylene, chlorosulfonated polyethylene styrene, and creosote Indeed, creosote itself comprises about 85% PAHs

Thermal degradation of bisphenol A epoxy resin, creosote, cross-linked polyethylene, Kapton, Nomex, polyethylene, polyethylene terephthalate (Mylar), polystyrene, and polyurethane gives other toxic semivolatile or solid products of concern. These are aromatic amines, phenolic compounds, or aromatic hydrocarbons. Other materials reviewed include neoprene, six fluorinated polymers, four nylons, dicyandiamide (no thermal-degradation information, however), nitrile rubber, polysulfone kraft paper, and cross-linked polyethylene.

One appendix of the report summarizes the more toxic degradation products from materials reviewed either in this report or in a previous EPRI-sponsored literature search. In addition, degradation products from other materials not covered in detail in this review are also summarized in the first appendix. Another appendix lists the relative volatility, inhalation limits, and other health and safety information for most of the more than 200 thermal-degradation products listed.

EPRI PERSPECTIVE

This report was initially undertaken as the first quarterly report for EPRI research project RP2028-15. However, because of its excellent makeup, it was expanded for publication as an interim report.

In addition to its use in selecting priorities for subsequent laboratory research, this information should also provide many insights to utility environmental engineers for expanding their knowledge of commonly used materials. One caveat must be observed. There was no effort to categorize materials based on quantity usage.

PROJECT

RP2028-15
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EL-4939
Research Project 2028-15

Interim Report November 1986

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ABSTRACT

The published literature, primarily from 1967 to the present, is reviewed on the pyrolysis, combustion, or other thermal degradation of 26 utility materials. These materials include polymers, rubbers, adhesives, films, fluids, coatings, and miscellaneous materials. The materials are used for electrical insulation or construction (gaskets, wood preservation, etc.) Materials reviewed are grouped according to their chemical composition, that is, by whether they contain chlorine, fluorine, nitrogen, sulfur, or only carbon, hydrogen, and/or oxygen.

Pentachlorophenol and its sodium salt produce polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) Several polycyclic aromatic hydrocarbons (PAHs), many of which are known carcinogens, are produced from combustion or pyrolysis of polyethylene, chlorosulfonated polyethylene, styrene, and creosote Indeed, creosote itself comprises about 85% PAHs Thermal degradation of bisphenol A epoxy resin, creosote, crosslinked polyethylene, Kapton, Nomex, polyethylene, poly(ethylene terephthalate) (Mylar), polystyrene, and polyurethane gives other toxic semivolatile or solid products of concern. These are aromatic amines, phenolic compounds, and/or aromatic hydrocarbons. Other materials reviewed include neoprene, six fluorinated polymers, four nylons, dicyandiamide (no thermal degradation information, however), nitrile rubber, polysulfone, kraft paper, and crosslinked polyethylene.

One appendix summarizes the more toxic degradation products from materials reviewed either in this report or in a previous EPRI-sponsored literature review In addition, degradation products from other materials not covered in detail in this review are also summarized in the first appendix Another appendix lists the relative volatility, inhalation limits, and other health and safety information for most of the more than 200 thermal degradation products listed

ACKNOWLEDGMENTS

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TABLES

SUMMARY

This report presents a review of the literature on the thermal degradation of a large number of materials used by and of interest to electrical utilities. This review supplements a previous Electric Power Research Institute (EPRI) literature review (EPRI Report No. EL-4503) on the thermal degradation products from PCB substitute fluids. This review will assist utilities in the evaluation of potential hazards of equipment and materials in fire situations. It will also assist scientists in the design of laboratory experiments in the projects to be done at MRI (RP2028-15) and at the University of Dayton Research Institute (UDRI) (RP2028-16) to fill some of the gaps in the literature.

A computerized search of Chemical Abstracts back to 1967 was performed for about 50 utility materials. Useful information was retrieved for about half. The EPRI utility advisors to this project were also canvassed for their recommendations of candidate materials. Materials containing chlorine, fluorine, nitrogen, and sulfur atoms were initially selected for in-depth review because of the dangers associated with their volatile thermal decomposition products, the simplest of which are hydrogen chloride, hydrogen fluoride, hydrogen cyanide and nitrogen oxides, and sulfur dioxide, respectively. However, the volatile products are of lesser concern as building and environmental contamination problems after a fire involving electrical equipment than the products of low volatility (boiling point above about 130°C). Materials containing only carbon, hydrogen, and/or oxygen atoms were therefore reviewed because of their potential, like that of fossil fuels and cellulose-based fuels, for forming carcinogenic polycyclic aromatic hydrocarbons (PAHs) during thermal degradation. Two utility materials, polychlorinated biphenyls (PCBs) and poly(vinylchloride) (PVC), are briefly reviewed as benchmarks for comparison with the other materials reviewed.

Data from the primary literature on combustion (heating in air or oxygen) or pyrolysis (heating in nitrogen, helium, or other inert atmosphere) of the materials were compiled on an experiment-by-experiment basis and then summarized. Data were also compiled from secondary sources on the occupational exposure limits in air and the health effects of most of the more than 200 decomposition products identified.

the materials reviewed may form highly toxic carbon monoxide during combustion Other products identified as being potentially among the most hazardous thermal degradation products of the materials reviewed are grouped by toxic action in Table S-1

Table S-1 may be helpful in evaluating the relative hazard of burning these materials, with four caveats. Since the table was compiled without reference to the relative amounts produced, it cannot be used to tell which particular component(s) would be most likely to be responsible for the short-term or the long-term effects Perhaps a larger amount of a less toxic material may determine the toxicity of the total degradation products; in other words, "the dose makes the poison " One must also remember when examining Table S-1 the uneven characterization of the thermal degradation products of the materials. For example, thermal degradation products of polystyrene have been much more thoroughly characterized then those from polysulfone. The mere numbers of toxic products listed for the various materials, therefore, cannot be used to judge their relative hazard. Also, as was noted for formulated neoprene, these materials in actual use will have been compounded with plasticizers and other materials whose decomposition products may be as important as those from the virgin, unformulated material. Finally, there has been no attempt to provide perspective on the relative quantities of the materials used in utility systems. In many cases, the amounts manufactured and used for other purposes completely outweigh any quantities used by electric utilities.

The following sections summarize the degradation products found in the literature for the utility materials. As with the body of the report, the materials are grouped by chemical composition, with materials containing fluorine, chlorine, nitrogen, and sulfur discussed in separate sections before the one discussing materials containing only carbon or hydrogen or carbon, hydrogen, and oxygen Not all products are mentioned in this summary, nor are the conditions for formation given in as much detail as in the body of the report. Remember that the products of thermal degradation are highly dependent on the conditions pyrolysis vs combustion, heating rate, final temperature, amount of material, presence of additives, and other factors.

Table S-1

HAZARDOUS THERMAL DECOMPOSITION PRODUCTS (OTHER THAN CARBON MONOXIDE) FROM MATERIALS REVIEWED

Material Degraded	High Acute Systemic Toxicity[a]		Severely Irritating to Eyes, Skin, or Respiratory Tract		Carcinogenic		Reproductive Hazard (Mutagen, Teratogen, Other)	
	Volatile[b]	Semi- or Nonvolatile[c]	Volatile	Semi- or Nonvolatile	Volatile	Semi- or Nonvolatile	Volatile	Semi- or Nonvolatile
Chlorine Containing Materials								
Neoprene (cured, most identified degradation products are from additives)	HCN H_2S SO_2		HCl SO_2	Nonylphenol Phthalic anhydride			SO_2 Toluene	
Pentachlorophenol					Benzene	Hexachlorobenzene Octachlorodibenzo-p-dioxin 2,3,7,8-tetrachlorodibenzo-p-dioxin		
Fluorine Containing Materials								
Halar (also contains Cl)	HF		HCl HF					
Teflon	Polytetrafluoroethylene decomposition products (Teflon fume)		SiF_4[d]		Teflon fume			
Teflon FEP			SiF_4[d]					
Tefzel	HF		HF		Vinylidene fluoride			
Viton	HF		HF		Vinylidene fluoride			

(continued)

Table S-1 (continued)

Material Degraded	High Acute Systemic Toxicity[a]		Severely Irritating to Eyes, Skin, or Respiratory Tract		Carcinogenic		Reproductive Hazard (Mutagen, Teratogen, Other)	
	Volatile[b]	Semi- or Nonvolatile[c]	Volatile	Semi- or Nonvolatile	Volatile	Semi- or Nonvolatile	Volatile	Semi- or Nonvolatile
Nitrogen Containing Materials								
Creosote (also contains S)		o-Toluidine p-Toluidine Xylidine		Cresol Naphthalene α-Naphthol Phenol Quinoline α-Toluidine p-Toluidine		Benz[a]anthracene 7,7-Benzofluoranthene Benz[j]fluoranthene Benzo[b]fluoranthene Benzo[a]pyrene Benzo[e]pyrene (suspect) Chrysene (suspect) Dibenz[a,h]anthracene Fluoranthene Naphthalene (suspect) α- and β-Naphthylamines (suspect) Phenol (suspect) 2,3-α-Phenylenepyrene α-Toluidine (suspect)		Acenaphthene Acenaphthylene Benzo[k]chrysene Benzo[j]fluoranthene Benzo[b]fluoranthene Dibenz[a,h]anthracene α-Naphthol Perylene 2,3-α-Phenylenepyrene Quinoline α-Toluidine 2,4- and 2,5-Xylidines
Kapton	HCN	Aniline Phenol		Phenol				
Nitrile rubber	Acetonitrile HCN		Ammonia		Acrylonitrile (suspect)	Styrene	Toluene	
Nomex	Acetonitrile Cyanogen HCN Nitric oxide	Aniline Phenol Xylidine	Acetaldehyde Acetic acid Ammonia	Benzoic acid Phenol α-Tolunitrile	Acrylonitrile (suspect) Benzene 1,3-Dioxane	Aniline (suspect) Phenol (suspect)	H_2O Toluene	
Nylon 6,6	HCN							
Polyurethane (ether or polyol) and toluene diisocyanate	Acetonitrile HCN		Acetaldehyde Ammonia Ethyl alcohol	2- or 4-Methylpyridine Quinoline Toluene 2,4-diisocyanate	Acrylonitrile Benzene	Styrene 2,4-Toluene diamine	H_2O Toluene	Quinoline

Table S-1 (continued)

Material Degraded	High Acute Systemic Toxicity[a]		Severely Irritating to Eyes, Skin, or Respiratory Tract		Carcinogenic		Reproductive Hazard (Mutagen, Teratogen, Other)	
	Volatile[b]	Small or Nonvolatile[c]	Volatile	Small or Nonvolatile	Volatile	Small or Nonvolatile	Volatile	Small or Nonvolatile
Silica Containing Material								
Chlorosilicated polyethylene	SO_2		HCl SO_2	Naphthalene	Benzene	Naphthalene (suspect) Styrene	SO_2 Toluene	Acenaphthene Acenaphthylene
Polysulfone	SO_2	Cresol Phenol	SO_2	Naphthalene Phenol Trimethyl benzene	Benzene	Naphthalene (suspect) Phenol (suspect) Styrene	SO_2 Toluene	
Material Without Heteroatoms								
Bisphenol A epoxy (may contain Cl)	Methyl chloride	Cresol Phenol		Naphthalene Phenol	Benzene	Naphthalene (suspect) Styrene	Toluene	
Uncrosslinked polyethylene (see also products from polyethylene)		Phenol		Phenol	Benzene Chloroform	Phenol (suspect)	Toluene	
Polyethylene	Acrolein Furan		Acetaldehyde Acetic acid Acrolein Butyraldehyde Ethyl alcohol Formaldehyde Formic acid Isobutyraldehyde Valeraldehyde	Acrylic acid Butyric acid Naphthalene	Benzene 1,3-Butadiene Formaldehyde	Benz[a]anthracene 2,3-Benzofluoranthene Benzo[c]phenanthrene Benzo[a]pyrene Benzo[e]pyrene (suspect) β-Butyrolactone Chrysene Fluoranthene Naphthalene (suspect)	Acrolein Ethyl alcohol Formic acid Tetrahydrofuran Toluene	Butyric acid Methylphenanthrene

(continued)

Table 5-1 (continued)

Material Degraded	High Acute Systemic Toxicity[a]		Severely Irritating to Eyes, Skin, or Respiratory Tract		Carcinogenic		Reproductive Hazard (Mutagen, Teratogen, Other)	
	Volatile[b]	Semi or Nonvolatile[c]	Volatile	Semi or Nonvolatile	Volatile	Semi or Nonvolatile	Volatile	Semi or Nonvolatile
Material Without Heteroatoms (continued)								
Polyethylene terephthalate) (Mylar)	Acrolein		Acetaldehyde Acrolein Formaldehyde	Benzoic acid Naphthalene	Benzene Formaldehyde	Naphthalene (suspect) Styrene	Acrolein Toluene	
Polystyrene		Phenol	Acetaldehyde Acetic acid Formaldehyde Formic acid	Naphthalene Phenol	Benzene Formaldehyde	Benz[a]anthracene Benzo[c]phenanthrene Benzo[e]pyrene (suspect) Chrysene 3 Methylcholanthrene Styrene Naphthalene (suspect) Phenol (suspect)	Toluene	Acenaphthene Benzo[g,h,i]-perylene 3 Methylcholanthrene

[a] Products in this column were selected from among those in Appendix B whose oral LD_{50} dose (lethal dose killing half of the test animals) is < 50 mg/kg body weight (but, whose inhalation LD_{50} is < 100 ppm in air for an exposure period of 8 hr or less, and/or whose dermal LD_{50} is < 43 mg/kg bw

[b] Volatile compounds are defined for the purposes of this study as those compounds with boiling points less than 130°C These compounds are gases (e.g., CO) or liquids (e.g. benzene) that would evaporate rapidly and not leave a residue after a fire

[c] Semivolatiles and nonvolatiles are defined for purposes of this study as compounds with boiling points greater than 130°C these compounds are liquids (e.g. styrene) or solids (e.g., PAHs) with low vapor pressures and would not be expected to evaporate quickly from a fire residue The demarcation between the two classes is somewhat arbitrary and is necessarily imprecise, for example, toluene (b.p. 111°C) is categorized as a volatile while styrene (b.p. = 145°C) is categorized as a semivolatile

[d] HF released from the polymer or from the polymer and moisture, reacts with glass in the sampling and analytical apparatus to give the artifact SiF_4

CHLORINE-CONTAINING MATERIALS

Thermal degradation of chlorine-containing materials releases long-term residual contaminating products as well as the more immediately hazardous volatiles Fires involving PCBs in electric equipment have contaminated buildings with polychlorinated dibenzofurans (PCDFs) and, sometimes, when chlorinated benzenes were present, with polychlorinated dibenzo-p-dioxins (PCDDs). Incinerator emissions of PCDFs and PCDDs have been ascribed to the widely used utility insulation material PVC Previous reviews on the combustion of PCBs and PVC were briefly summarized. Chlorinated materials reviewed in detail in this section were neoprene (polychloroprene) and pentachlorophenol

Neoprene rubbers are used to coat electric wiring and as cable jackets All of the neoprene materials reviewed were cured and compounded with numerous additives Practically all of the thermal decomposition products appeared to be derived from the phthalate plasticizers, although the long-chain hydrocarbon fragments may have come from the polymer itself Among the products identified were hydrogen cyanide (HCN), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), nonylphenol, phthalic anhydride, and toluene.

Pentachlorophenol is used to preserve wood construction materials, including utility poles. Combustion of pentachlorophenol and its sodium salt gave octa-, hepta-, hexa-, and lower chlorodibenzo-p-dioxins in the volatiles and residues Octa- and hexachlorodibenzofuran were also identified. Other combustion products identified were penta- and hexachlorobenzene and decachlorobiphenyl

FLUORINE-CONTAINING MATERIALS

The fluorinated polymers reviewed include Halar (which also contains chlorine), Teflon, Teflon FEP, Teflon PFA, Tefzel, and Viton These materials are used as wire and cable insulation. Combustion and pyrolysis products reported generally included monomers and other fluorinated C_1 to C_4 alkanes, alkenes, or cycloalkanes, and hydrogen fluoride (HF) or silicon tetrafluoride (SiF_4) (presumably formed from reaction of fluoride and glass of the experimental apparatus) Carbon monoxide (CO), carbon dioxide (CO_2), carbonyl fluoride (COF_2), and trifluoroacetyl fluoride (CF_3COF) were the oxygen-containing products usually reported, although unidentified aldehydes, alcohols, and carboxylic acids were detected among the Halar combustion products Vinylidene fluoride, which was emitted from thermal degradation of Viton as well as from Tefzel, and Teflon fume were other pyrolysis or combustion products

NITROGEN-CONTAINING MATERIALS

Materials considered in this section include creosote; the paper-impregnating substance dicyandiamide (cyanoguanidine, colloquially called "dicy"), the polyether imide Kapton; the aromatic polyamide Nomex, nitrile rubber, the four polyamides nylon 6, nylon 6,6, nylon 6,10, and nylon 11, and polyurethanes based on toluene diisocyanate and polyols.

Creosote used to protect utility poles from rot and worms is derived from coal tar It comprises about 85% PAHs, about 3 to 10% tar acids (phenolics); and the rest aromatic compounds containing nitrogen (N) (tar bases), oxygen (O), and sulfur (S) Individual PAHs released by burning creosote-treated railroad ties attained concentrations up to 0.3% in the solid particulates of the smoke. The carcinogenic PAHs identified were benz[a]anthracene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, and o-phenylenepyrene (indeno[1,2,3-cd]pyrene)

No information was found on the combustion or pyrolysis of dicyandiamide or of paper impregnated with dicyandiamide.

Kapton film is usad to insulate wire and cable, and Kapton molded parts and laminates may be used in printed wiring boards and integrated circuit carriers CO_2, CO, HCN, benzene, aniline, phenol, benzonitrile, dibenzofuran, phenyl isocyanate, substituted phthalimides and pyromellitimides, and a highly conductive char were produced by pyrolysis of Kapton.

Pyrolysis of nitrile rubber produced ammonia (NH_3), HCN, the monomers (acrylonitrile and butadiene), acetonitrile, other nitriles, various hydrocarbons, dimers, and trimers

Nomex paper is used to insulate dry-type transformers as well as to insulate high-performance motors and generators. Nomex is an aramid, that is, an aromatic polyamide prepared from 1,3-phenylenediamine and isophthalic acid or isophthaloyl chloride. Major inorganic pyrolysis products were CO_2, water (H_2O), CO, hydrogen (H_2), and HCN with minor amounts of ammonia, nitrous oxide (N_2O), and cyanogen Major organic pyrolysis products of Nomex were benzene, toluene (below 500°C), benzonitrile, 1,3-phenylenediamine, benzoic acid, aniline, 1,3-dicyanobenzene (above 500°C), and N-(3-aminophenyl)benzamide (600-700°C) The charred residue became more aromatic between 450 and 550°C By 1000°C, most of the hydrogen and oxygen had been lost from the char In contrast to pyrolysis, where 4 min at 1000°C

caused only 50% weight loss, no residue remained by 1000°C in air or oxygen Water, carbon dioxide, and/or carbon monoxide were major combustion products Nitric oxide (NO), nitrous oxide, HCN, cyanogen, benzene, substituted benzenes, acetone, acetaldehyde, benzoic acid, nitriles, 3-cyanobenzoic acid, alkanes, alkenes, and nitromethane were also identified among the Nomex combustion products

Nylons are used for plugs, connectors, wire jacketing, and many other electrical and electronic applications. In general, polyamides thermally degrade to give ammonia, nitriles, amines, cyclic ketones, esters, CO, CO_2, and monomers. Nylon 6 gives caprolactam oligomers, nylon 6,6 gives mainly cyclopentanone and less than 1% of the theoretically possible amount of HCN at temperatures around 700°C or higher Nylon 6,10 gives caprolactam, medium-length hydrocarbon chains (six to eight carbon atoms), and long-chain mono- and dinitriles. Nylon 11 behaves similarly on pyrolysis, hydrocarbons with six and seven carbon atoms being the most abundant

Polyurethane foams are being examined for use as insulating materials for cryogenic cables and underground transmission lines At temperatures below 800°C, polyurethanes pyrolyzed by giving off a yellow smoke containing all the nitrogen of the original material and comprising mainly polymeric isocyanates. The other volatile products formed at temperatures below 800°C included carbon oxides, nitrous oxide, alkanes, alkenes, and lower aldehydes and alcohols. Between 800 and 1000°C, nitriles, aromatic hydrocarbons, and aromatic N-containing heterocycles such as methylpyridine and quinoline were formed, although lower aldehydes and propene were still abundant at 1000°C. Other products at the higher temperatures included toluene diisocyanate, toluanediamine, and nitriles

SULFUR-CONTAINING MATERIALS

Chlorosulfonated polyethylene is generally crosslinked Its electrical uses include wire and cable coverings At temperatures below 600°C, major pyrolysis products were lower alkanes, lower alkenes, and toluene. By about 900°C, aromatic products predominated with high yields of benzene and naphthalene Styrene and several noncarcinogenic PAHs were found in the pyrolyzate Chlorosulfonated polyethylene may contain additives to reduce the amount of hydrogen chloride (HCl) emitted on combustion. Sulfur dioxide, which is highly toxic and irritating, is also evolved on combustion along with carbon oxides

Polysulfone (a copolymer of bisphenol A and 4,4'-dichlorodiphenylsulfone) has many electrical and electronic applications including connectors, TV components, capacitor film, and circuit boards. Combustion of polysulfone at 400°C caused a 70% loss in polymer weight but little smoke and little sensory irritation in rodents exposed to the volatile products. In a somewhat oxygen-deficient atmosphere, combustion at temperatures up to 750°C produced primarily CO, CO_2, sulfur dioxide, and a residue. Intermediate amounts of methane, benzene, and toluene were found with minor amounts of ethylene, ethane, ethylbenzene, and styrene.

MATERIALS CONTAINING ONLY C AND H OR C, H, AND O

Materials reviewed in this section included bisphenol A epoxy resins (although some are crosslinked with amines), crosslinked polyethylene, kraft paper, polyethylene, poly(ethylene terephthalate), and polystyrene

Epoxy resins are used as insulation in transformers and capacitors. New information on a common epoxy resin derived from bisphenol A and epichlorohydrin was examined and integrated with information from a previous review on epoxy resins (EPRI Report No. EL-4503). Decomposition products from combustion of a bisphenol A epoxy used in transformer coils included phenol, toluene, ethylbenzene, and benzene. Other experiments previously reviewed used different epoxy material or confounded the results by burning another fuel In these experiments, thermal decomposition products of novolak epoxies based on phenol-formaldehyde resins included phenol, cresol, and methyl chloride.

Crosslinked polyethylene has been used since the 1970s to insulate most of the distribution cables installed in the 15- to 46-kV range. Crosslinked polyethylene wire insulation was practically all volatilized by pyrolysis up to about 480°C Pyrolysis and combustion products have not been studied. Volatilization of decomposition products of impurities such as the chemical crosslinking agent dicumyl peroxide (DCP) might be expected during exposure to lower temperatures Decomposition products that have been identified from DCP included α-methylstyrene, cumene, phenol, and toluene

Kraft paper is used for insulation in oil-immersed equipment such as transformers Kraft paper pyrolysis gives the same products in about the same amounts as do other cellulosic materials (paper, wood, etc) Gases included the carbon oxides, hydrogen, acetylene, methane, ethylene, and other hydrocaroons Heating above 500°C gave lower molecular weight volatiles and char

A major use for polyethylene in the electric power industry in the United States is for duct or pipe for installing buried cable. Pyrolysis of polyethylene at temperatures up to 1000°C gave saturated hydrocarbons (paraffins, alkanes) and unsaturated hydrocarbons (olefins, primarily 1-alkenes with lesser amounts of α,ω-dienes) Combustion gave similar products, especially in the range 350 to 700°C Besides CO_2 and water, oxygen-containing products identified included alcohols, aldehydes, ketones, and carboxylic acids Aromatic product yields increased with increasing temperature, but yields of individual PAHs such as the carcinogen benzo[a]pyrene were only about 0 1% after incineration at 900°C. At 950°C, the concentrations of individual PAHs and other aromatics in cold-trapped condensates were less than 1 to about 4%

Poly(ethylene terephthalate) (PET, Mylar) is the most widely used film for electrical insulation Mylar film uses include barrier and insulation tape in cables and dielectric in high-temperature capacitors Major pyrolysis products included acetaldehyde, CO_2, benzoic acid, and vinyl benzoate and terephthalate. Lower amounts (1-9%) of CO, ethylene, and benzene and trace to minor amounts of alcohols, aldehydes, ketones, cyclic ethers, and hydrocarbons including benzene derivatives were detected Most of these were identified as combustion products along with dimers through pentamers of the original polymer

Polystyrene gave styrene as the major pyrolysis product in the volatiles at temperatures up to 1400°C Other major pyrolysis products included toluene, α-methylstyrene, cumene, and styrene oligomers Lower aliphatic aldehydes and carboxylic acids were major products along with benzene, toluene, ethylbenzene, styrene, and propylbenzene on combustion below about 500°C In one study, combustion at 800 to 900°C gave a soot in 50% yield. More than 100 compounds identified from polystyrene combustion at 800 to 950°C included many PAHs Several of the PAHs identified are carcinogens.

Section 1

INTRODUCTION

BACKGROUND

The overall goal of this project is to evaluate the potential of utility materials to generate toxic or otherwise undesirable thermal degradation products under fire conditions. Solid, liquid, and gaseous materials used by electric utilities could degrade under fire conditions and contribute to the toxic hazard. A wide variety of insulating and structural materials are of concern. The liquids of interest include PCB-substitute dielectric fluids for transformers and capacitors.

As part of the evaluation of these materials, this literature review has been conducted to supplement the literature review previously conducted by the Electric Power Research Institute (EPRI) (1). This review serves several purposes. The existing literature provides a great deal of information on the products of pyrolysis (thermal degredation in the absence of oxygen, usually in an inert atmosphere such as nitrogen or helium) and combustion (burning, thermal degradation in the presence of air or oxygen) and in itself is a valuable resource for utilities and electrical equipment manufacturers for evaluating potential hazards of equipment in fire situations. For work on this and the companion project at University of Dayton Research Institute (UDRI), the review clearly shows which materials have been studied in detail and which have not. Furthermore, the review gives a general indication of the products that may be anticipated from the laboratory experiments to be conducted on the current projects. Thus, Midwest Research Institute (MRI) (EPRI Project No. RP2028-15) and UDRI (EPRI Project No. RP2028-16) researchers can utilize this knowledge to design the experiments and also to specifically search for previously identified decomposition products.

This literature review also illustrates that the results of thermal decomposition experiments are highly dependent on the experimental conditions. Thus, comparisons of results from different studies will be difficult and will require great care to prevent overinterpretation of the data.

SEARCH STRATEGY

Chemical Abstracts Service Registry Numbers (CASRNs) were sought for all the materials listed in the RFP to avoid the use of numerous synonyms in a computerized search of Chemical Abstracts. CASRNs were found for most of the materials. Those CASRNs not readily available in printed lists were sought in the Registry File of CAS ONLINE. Each CASRN or compound name was coupled with a set of terms based on variations of the following words: pyrolysis, combustion, thermolysis, fire, burn, thermal degradation, thermal decomposition, and thermal oxidation. The search statements were used in the CA (Chemical Abstracts) File of CAS ONLINE. Abstracts were searched from 1967 to the present, except for polystyrene whose search was limited to the last 5 years because there was so much available literature.

Materials previously reviewed (1), those proposed for this review, and those actually completed in this review are identified in Appendix A. Initially materials known to release highly toxic volatiles (HCl, HF, HCN, NO_x, and SO_2) were selected for review. Later, materials with only C and H or C, H, and O atoms were examined for their potential to produce PAHs on exposure to elevated temperatures.

Pertinent articles were selected for compilation based on their abstracts. The articles were primarily English language, but Russian, German, and French articles were selected for acquisition if the methods used were likely to allow identification of specific decomposition products. A further selection process, based on the actual contents of the article, was performed when the documents were examined for data compilation.

DATA COMPILATION

Articles that did not identify the decomposition products (for example, those on thermal degradation analysis and differential scanning calorimetry that did not collect and analyze the volatile products emitted) were generally not examined closely. Combustion toxicity articles were sometimes useful in identifying at least relative amounts of carbon monoxide, carbon dioxide, and other toxic gases such as hydrogen cyanide or hydrogen chloride. Generally, the more recent articles and those that identified products by mass spectrometry were examined most closely and provided the most useful data.

Data sheets were used as a guide for extracting the information. Each pyrolysis or combustion experiment was described on a separate page using the same format.

In addition to the primary literature from which experimental and mechanistic details were extrected, various secondary sources were used such as the Modern Plastics Encyclopedia and the Encyclopedia of Polymer Science and Technology to supplement general handbook information on uses, structures, and electrical, other physical, and chemical properties. Some of this information was later used to prepare the text of this report.

Data for acute toxicity, carcinogenicity, and standards or recommendations for standards for workplace exposure in air were extracted for separate decomposition products from two sources: The OSHA Industrial Hygiene Technical Manual and the Registry of Toxic Effects of Chemical Substances These data are presented along with CASRNs and information on the relative volatility of most of the more than 200 thermal degradation products identified. Compiling data on the animal toxicity of the total volatile and particulate material released during standardized combustion or pyrolysis tests of the subject materials is beyond the scope of this review. Data are not directly comparable among the studies and would require extensive critical review.

CONTENTS AND ORGANIZATION OF THE REPORT

The remainder of this report contains profiles for each material organized as follows General Information, Thermal Decomposition Mechanisms (not always present), a Summary of Experimental Studies Reviewed subdivided into separate discussions for pyrolysis and combustion (when information was available on both processes), and the References citec. The materials are grouped by type of hetero atom present in their molecules Thus, Section 2 contains profiles for chlorine-containing polymers such as neoprene, Section 3 is on the fluorine-containing materials. Section 4 is on materials containing nitrogen atoms, and Section 5 contains information on two polymers containing sulfur atoms. Section 6 contains profiles on materials that contain only C and H or whose only other component is oxygen.

Appendix A includes the materials proposed for review or previously reviewed and their most toxic degradation products, if any thermal degradation literature was available More then 200 products were identified for the 26 materials profiled Appendix B contains toxicity, stanoards, and physical state information for most of these products The starting material(s) for each product are identified

REFERENCE

1 J. V. Zbozinek, J. R. Marsh, D Guth and A. Bohrnerud (SCS Engineers, Inc) State-of-the-Art Review of Combustion and Pyrolysis By-Products of PCB Substitutes EPRI Report No. EL-4503. Palo Alto, Calif Electric Power Research Institute, March 1985

MONS 020434

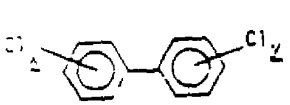
Section 2

CHLORINE-CONTAINING MATERIALS

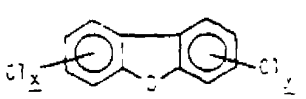
BACKGROUND INFORMATION ON TWO WELL-STUDIED CHLORINATED COMPOUNDS (PCBs and PVC)

Polychlorinated biphenyls (PCBs) and poly(vinyl chloride) (PVC) are two widely used utility materials whose thermal decompositions have been extensively studied and reviewed. Although PCBs and PVCs are not primary subjects of this literature review, work on these materials is briefly summarized here to provide a basis for comparing their thermolysis products with those from the other materials reviewed in this report.

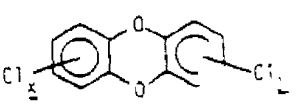
The Electric Power Research Institute (EPRI) has an extensive ongoing research program to determine the degree of the utility industry problem regarding PCBs, polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). Among these are pyrolysis and combustion studies of PCBs and PCB-contaminated fluids such as mineral oils. This effort is supplemented by reviews and experimental work on the pyrolysis and combustion of PCBs and other utility materials (1). The recent NIOSH Current Intelligence Bulletin 45 Polychlorinated Biphenyls (PCBs): Potential Health Hazards from Electrical Equipment Fires or Failures (2) and two EPRI-sponsored reviews on PCBs (3) and other materials (4) form the basis for most of the following discussions on PCBs and PVC.



PCBs



PCDFs

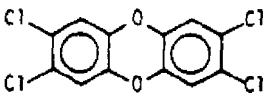


PCDDs

Polychlorinated Biphenyls (PCBs)

The NIOSH Current Intelligence Bulletin 2) gives guidelines to protect the health of emergency response and cleanup workers in the aftermath of PCB-containing electrical equipment fires that have produced widespread building contamination

with PCBs, PCDFs, and PCDDs. NIOSH recommends that PCBs and 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) be regarded as potential human carcinogens In addition, PCBs, PCDFs, and/or PCDDs have been reported to injure the liver, thymus, and reproductive systems of test animals and to produce chloracne, numbness of the limbs, and other adverse effects in humans (2).

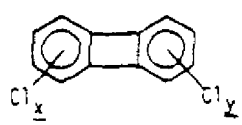


2,3,7,8-TCDD

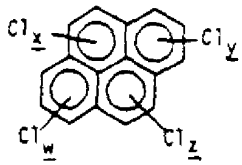
Between 1932 and 1979, when the U.S Environmental Protection Agency (EPA) issued restrictions on the manufacture and commercial use of PCBs, 135,000 PCB-containing transformers were put into service. Many of these transformers and PCB-containing capacitors are still in use. EPA estimated that by the end of 1984, approximately 107,000 PCB-containing transformers were in use or being stored for reuse, more than two-thirds of these transformers were used in or near public buildings As a result of the mandated selective EPA phase-out schedules, these numbers have decreased significantly. In 1981 there were about 3.3 million capacitors containing more than 3 lb (0.7 kg) PCBs. In addition, past manufacturing and transformer servicing practices have contaminated mineral oil-filled equipment with trace amounts of PCBs (2,3).

Some commercial PCB mixtures manufactured in the United States contained up to 6 ppm PCDFs, and PCBs from Europe and Japan contained up to about 20 ppm PCDFs (3) PCDFs have been found in almost all measurements of contamination after fires in electrical equipment containing PCBs. A total of 2,163 ppm PCDFs was determined in soot from the combustion of transformer fluid comprising PCBs and chlorinated benzenes during the Binghamton (New York) State Office Building fire (2,3)

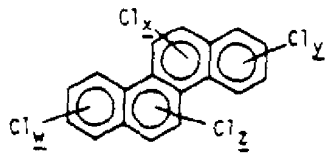
The NIOSH document summarizes the concentration of PCBs, PCDDs, and PCDDs in the soot and surface wipes after 11 U S. fires involving electrical capacitors or transformers. PCDDs were found in the soot from five of these fires in concentrations ranging from 0.16 to 19.9 ppm. The highest level was from the Binghamton fire (2). Other chlorinated aromatics detected (but not quantitated) from fires involving PCB-containing electrical equipment were polychlorinated biphenylenes (PCBPs), polychlorinated pyrenes (PCPYs), and polychlorinated chrysenes (PCCYs) Some PCB samples themselves contain PCBP, PCPYs, and PCCYs (3)



PCBPs



PCPYs



PCCYs

Neither ordinary working conditions nor long-term overload (180°C maximum damages the insulation rapidly) for electrical equipment containing PCBs is conducive to formation of PCDDs and/or PCDFs. Optimum conditions for formation of PCDFs from PCBs are 8% excess oxygen and about 675°C for at least 0.8 sec. These conditions produced percent levels of PCDFs (relative to the amount of PCBs combusted) from mineral oil or silicone oils contaminated with at least 5 ppm PCBs (5).

The major combustion products formed from fires starting as a result of arcing in airless transformers or capacitors are PCBPs. PCDFs, PCPYs, and PCCYs are also detected. PCBPs do not form in externally initiated fires; PCDFs are the major product with smaller amounts of PCPYs and PCCYs. PCDDs form only if chlorobenzene or chlorophenols are present in the transformer askarel (2) since formation from a PCB would require breakage of the biphenyl link.

Other known or suspected environmental sources of PCDDs and PCDFs include the manufacture of trichlorophenoxyacetic acid (2,4,5-T), pentachlorophenol, and other chlorinated phenols; municipal and industrial incineration of chlorinated compounds and plastics and bleached and unbleached paper, copper smelting, steel production, and, to a lesser degree, fuel combustion in coal-fired power plants and wood and peat burners (6)

Poly(vinyl chloride) (PVC)

The pyrolysis and combustion of PVC [$\leftarrow CHClCH_2 \rightarrow_n$] and PVC formulations with stabilizers, plasticizers, fillers, dyes, and other additives have been studied extensively Two recent books review thermal degradation of PVC (7,8) Benzene and hydrogen chloride are the major pyrolysis products. Other pyrolysis products identified in the range 400 to 800°C are toluene, ethylbenzene, o-xylene, styrene, naphthalene, 2-methylnaphthalene, chlorobenzene, o- and p-dichlorobenzene, and 1,2,4- and 1,3,5-trichlorobenzene (4) Only trace amounts of chlorobenzenes and other chlorine-containing hydrocarbons are formed during PVC pyrolysis (9)

Degradation products are similar for pyrolysis and combustion except that combustion gives CO, CO_2, and H_2O. Very small amounts of vinyl chloride are evolved The major aliphatic compounds, formed in very small amounts, are C_1 to C_6 alkanes and alkenes (8)

Combustion of PVC mixed with wood chips in the range 570 to 1130°C produced chlorinated benzenes, octachlorostyrene, and PCBs. Combustion and arcing produced phosgene $(COCl)_2$ (4)

Chlorinated benzenes are known precursors of PCDDs and PCDFs Other chlorinated polyaromatic hydrocarbons (PAHs) might also be expected to form, and PVC is a suspected source of the PCDDs and PCDFs found in municipal and industrial incinerator emissions (3) Conflicting reports have appeared in the literature Rappe and coworkers (10,11) reported that PVC pyrolysis produced hexa- and hepta-CDDs, PCDFS containing 4 to 7 Cls, and other PCDDs and PCDFs. The total amount of PCDDs and PCDFs produced at 800°C was about 1 ppm based on the weight of PVC However, Karasek and coworkers (12) reported in 1983 that neither the concentrations nor the pattern of separate PCDDs and PCDFs in the fly ash from an energy-recovering municipal incinerator changed significantly by adding three times as much PVC as usual to the incinerator feed. Such results do not support the contention that PVC is a direct source of PCDDs and PCDFS in incinerator emissions. In fact, in 1984 Karasek and coworkers (13) stated that neither of the two chlorinated aromatics detected by gas chromatography-mass spectrometry after combustion of PVC under incinerator conditions at 800 to 950°C had chlorine atoms attached to an aromatic nucleus. The two chlorinated alkylbenzenes detected were chlorinated on the alkyl side group. Among the PAHs found were acenaphthylene, anthracene, benz[a]anthracene, benzo[j]fluoranthene, benzo[c]phenanthrene, benzo[a]pyrene, benzo[e]pyrene, biphenyl, chrysene, dihydroanthracene, fluorene, fluoranthene, indene, phenanthrene, pyrene, and methyl- and phenyl-substituted derivatives of the preceding compounds The only oxygen-containing species reported was phenol Octachlorodibenzo-p-dioxin was specifically sought and not found, although no detection limit was given. PVC might supply the chlorine needed to produce chlorinated phenols, which are more likely direct PCDD precursors than PVC or chlorinated benzenes Combustion of vegetable materials (presumably the phenol source in municipal refuse) with PVC or other chlorine source has been reported to give emissions containing chlorophenols, PCDDs, and PCDFs (14)

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MONS 020439

NEOPRENE

CASRN. 9010-98-4

Synonyms Polychloroprene; Poly(2-chloro-1,3-butadiene), Neoprene GN (same as GR-M--government rubber, monovinylacetylene) Neoprene G types (interpolymerized, with sulfur and contain a thiuram stabilizer), W types (no sulfur or thiuram) (1)

Insulation Materials: Neoprene-118 (multiconductor power cable), Neoprene-84 (single-conductor high-voltage cable); Neoprene-007 (welding cable), Neoprene-435 (high-voltage, high-amperage cable) (2).

Trade Names (producers) DuPrene (DuPont)

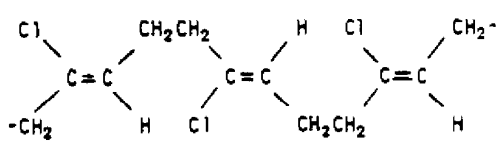
General Information

Molecular Formula: $(C_4H_5Cl)_n$

Structure of Monomers and Polymer.

$CH_2:CClCH:CH_2$

2-chloro-1,3-butadiene; chloroprene



Neoprene (head-to-tail)

Trans structure shown is consistent with x-ray diffraction fiber analysis (3)

Cis-1,4-polymerization, 1,2-polymerization, and 3,4-polymerization give small amounts of other structures. About 5% is present in neoprene polymerized at -40°C, ~ 30% at 100°C.

About 10 to 15% each of "head-to-head" and "tail-to-tail" moieties are present in a typical polychloroprene according to NMR evidence (1)

Uses Neoprene is used for wire and cable belts, hose, extruded goods, coatings, molded and sheet goods, adhesives, automotive gaskets and seals, petroleum and chemical tank linings (4), and coatings for electric wiring (5) Neoprene is not

suitable as electrical insulation, but it is used as a cable jacket because of excellent resistance to light, moisture, fire, chemicals, and oils. Neoprene cable jackets replace the cotton braids, natural-rubber jackets, and lead sheaths formerly used on rubber cables. However, chlorosulfonated polyethylene is preferred for cables for fixed installations (6).

Neoprene has several shortcomings, including greater expense and lower chemical resistance than poly(vinyl chloride) or polyethylene, as a cable sheath material (7). However, neoprene has apparently found some commercial use in multiconductor power cable; single-conductor high-voltage cable; high-voltage, high-amperage cable, and welding cable (2).

Thermal Decomposition Mechanisms

No information was found on unformulated neoprene. Neoprene formulations give the largest variety of pyrolysis products at a radiant flux of 5 W/cm^2. Cyclic and heterocyclic compounds, some with nitrogen in the ring, predominate and originate from decomposition of plasticizers. At a radiant flux of 8 W/cm^2, liquid degradation products decrease. Aromatic compounds are formed by cracking of the polymer followed by recombination of smaller into larger hydrocarbons. HCl evolution is retarded by the presence of basic additives. Neoprene formulations form a char layer during burning at a faster rate at higher radiant flux exposures, possibly insulating the material from rapid degradation (2).

Summary of Experimental Studies Reviewed

Pyrolysis. Pyrolysis of a cured neoprene rubber used as a hose cover gave the following mass spectral peaks (percent relative intensity) attributed to the neoprene: 36 (~ 14%, HCl), 38 (~ 6%), 88 (~ 12%; monomer), 90 (< 6%), 141 (~ 3%), 176 (~ 3%, dimer), and 178 (~ 3%). Dioctyl phthalate plasticizer and phenyl-β-naphthylamine were also identified (8). Pyrolysis of a W-type (no sulfur) neoprene at temperatures up to 300°C gave ions with mass peaks arranged in order of increasing intensity: 55, 91, 67, 69, 81, 73, 129. A G-type (sulfur-containing) neoprene pyrolyzed at temperatures up to 350°C gave ions with mass peaks: 53, 91, 88, 105, 77, 141 and 79; at temperatures up to 430°C, the peaks were 91, 41, 105, 129, 141, 165 and 179. Peaks found at 239 and 285 were attributed to the presence of resin and peaks at 60, 73, and 254 were due to fatty acid processing agents (9). Pyrograms (gas chromatographic peaks) have been published (10,11), but products were not identified.

Combustion Virgin neoprene began to decompose at 240°C when heated at the rate of 40°C/min The weight loss due to HCl and other volatile decomposition products was 45%, no char formed. Under these conditions, various formulated neoprene insulation materials showed 18 to 46% weight loss due to HCl and other volatiles and formed a char representing 6 to 48% of the original weight (2).

Alvares et al (1983) (2) identified products from combustion of a formulated neoprene insulation material. Many of the products were probably due to decomposition of the phthalate plasticizer Products evolved during dehydrochlorination included 1-octanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$, assuming a straight chain), phthalic anhydride, nonylphenol ($C_9H_{19}C_6H_4OH$), dioctyl phthalate, 4,5-dimethyl-1-α-p-methoxybenzoyloxy-p-methoxybenzylidene-1, 11-N-dicyclocosane [sic], n-nonacosane, 2-(methylthio)benzothiazole, 3-ethyl-5-(2-ethylbutyl)octadecane, n-heptacosane, 1-methylbutyl isobutyrate, and phthalanil. Products evolved after dehydrochlorination included n-hexadecane, squalene, dioctyl phthalate, diisobutyl phthalate, palmitic acid, 7-n-butyldocosane, 3-ethyl-5-(2-ethylbutyl)octadecane, and norpentylthiol [sic] acetate.

Products from combustion at 200 to 800°C identified in the air of a combustion toxicity chamber were 5,510 ppm carbon monoxide (CO) and 3,170 ppm methane (CH_4), with a char yield of 34.3% (12). (The combustion products killed the test animals within 25 min compared to 15 min for Douglas fir.) CO and HCl were major products from flaming combustion of neoprene seat padding and hose materials HCN was a minor product. SO_2 and H_2S in minor amounts were evolved from the neoprene sample that had apparently been vulcanized with sulfur (13)

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PENTACHLOROPHENOL

CASRN 87-86-5 (Na salt: 131-52-2)

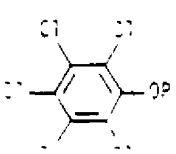
Synonyms Penta; PCP, penchlorol, salt Na pentachlorophenoxide

Trade Names (producers) Santophen 20, salt Santobrite, Dowicide G

General Information

Molecular Formula C_6HCl_5O, mol. wt 266.35
C - 27.05%, H - 0.38%, Cl - 66.56%, O - 6.01%

Structure

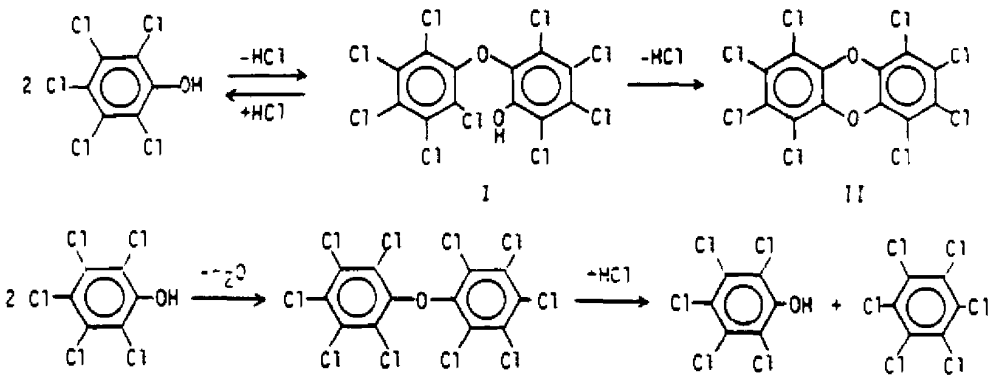


where R = H or Na

Uses Bactericide, fungicide, and slimicide, primarily used to preserve wood, wood products, and other materials. It has also been used as an herbicide, insecticide, and molluscicide (1).

Thermal Decomposition Mechanisms

The following equations represent reactions leading to polychlorinated diphenyl ethers, octachlorodibenzo-p-dioxin, and hexachlorobenzene from pentachlorophenol (2).



Summary of Experimental Studies Reviewed

Pyrolysis Thermal decomposition of bulk PCP at 250°C for about 12 hr in a sealed tube gave ~ 50% conversion, primarily to 2-(2',3',4',5',6'-hexachlorophenoxy)-3,4,5,6-tetrachlorophenol (I) plus small amounts of octa-CDD (II); Na PCP reacted at 360°C within about 20 min to give 100% octa-CDD (3).

Combustion. Technical grade pentachlorophenol (PCP) or its sodium salt (Na PCP) may contain chlorinated dibenzo-p-dioxins (CODs) (hexa-, hepta-, and octa-). Combustion experiments almost always give detectable octachlorodibenzo-p-dioxin (octa-CDD) In experiments burning technical pentachlorophenol at 515 to 800°C, with controlled amounts of O_2, maximum amounts of hepta- and octa-CDD formed at the lowest temperature; the amount of hexa-CDD was somewhat higher at higher temperature Higher amounts of CODs were formed during open burning (mostly hepta- and octa-CDD) With only 1 5% O_2, almost twice as much total CDDs was formed at 660°C as from open burning. Major products in reduced oxygen atmospheres were penta- and hepta-CDDs, the level of TCDD (tetra-CDD) was higher than from the other experiments (4) Open burning of a pure Na salt of pentachlorophenol gave octa-, penta-, and hexa-CDDs in sharply decreasing amounts (5) Combustion results were

compared for materials (wood or paper) treated with pure Na salt, impure Na salt, or pentachlorophenol The highest amounts of octa-CDD were in combustion products of the Na salt-treated materials, but in the burned residues, high amounts of octa-CDD were found in the PCP-treated samples. Amounts of unburned residue were higher at lower temperatures (6)

A 1985 report of an analysis of combustion products at 600°C by high resolution gas chromatography-mass spectrometry (HRGC-MS) listed the following products: octa-CDD, octa- and hexachlorodibenzofuran, decachlorobiphenyl, octachloronaphthalene, pentachlorobenzene, hexachlorobenzene, and products identified only by formulas--C_9Cl_8O, $C_{10}Cl_8O$, and $C_{14}Cl_{10}O$ (7). These latter formulas may be only fragments 2,3,7,8-TCDD was specifically said to be absent, but the only CDD detected was the CDD usually present in the highest amounts: octa-CDD

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Section 3

FLUORINE-CONTAINING MATERIALS

HALAR

CASRN 25101-45-5

Synonyms. 1.1 Ethylene-chlorotrifluoroethylene copolymer; ECTFE.

Trade Names (producers). Halar (Allied Chemical); General Purpose Halar 300 or 500 or 502 [but Halar 200 is poly(chlorotrifluoroethylene), CASRN 9002-83-9], Halar 555 (blown).

General Information

Molecular Formula. $(C_4H_4ClF_3)_n$

Structure of Monomers and Polymer:

$$CH_2{:}CH_2 + CF_2{:}CFCl \longrightarrow -\left(CH_2CH_2CF_2\underset{Cl}{\underset{|}{C}}F\right)_n-$$

Uses The primary use of Halar is for wire and cable; other uses include injection molded products, tubing, binders, and coatings for chemical process apparatus Its biggest use in wire and cable is for plenum cable, coaxial cable, cable in mass transit cars, appliance wire, motor lead wire, and wire for lighting fixtures. Powders are used as binders for chlorine cell diaphragms and as mold release agents Film is used for cases for LiI pacemaker batteries, tapes for wire and cable insulation, and solar energy laminates Monofilament is used for mist eliminators, braided sleeving, and filter fabric (1). Halar is also used for nuclear control and instrumentation cable (it has excellent nuclear radiation resistance), back panel wire for computers and automatic telephone switching equipment, cathodic protection cable, and oil-well logging and submersible pump cable (2)

Thermal Decomposition Mechanisms

No specific information was found

Summary of Experimental Studies Reviewed

Pyrolysis No information was found on pyrolytic products from Halar.

Combustion No information was found on identified organics lost on combustion Thermal oxidation of a Soviet 1:1 ethylene-chlorotrifluoroethylene copolymer (m p 215°C) gave alcohols, aldehydes, and carboxylic acids at temperatures up to 275°C Long-term oxidation at 270°C caused profound destruction giving low molecular weight products with aldehyde and carboxy end groups (3).

Concentrations of HCl, HF, CO, and sometimes COF_2 generated in combustion toxicity experiments are too low to be the cause of the toxic symptoms observed in the test animals. Something other than these inorganics must cause the toxicity under some conditions (4).

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TEFLON

CASRN- 9002-84-0

Synonyms Polytetrafluoroethylene (PTFE), TFE, Polytef, Tetrafluoroethene homopolymer, Tetrafluoroethylene polymer, Polytetrafluoroethylene resin (1)

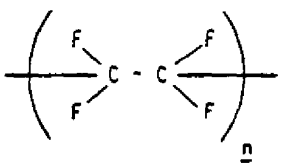
Trade Names (producers) Teflon (E I du Pont de Nemours), Fluon (ICI Americas) Fluoroflex (2), Halon (unfilled and filled) (Allied Corporation), Fluorocomp

(filled) (Liquid Nitrogen Processing Corporation); Tetraloy (filled) (ICI Americas); Hostaflon (Hoechst); Algoflon (Montedison), Soreflon (Ugine Kuhlmann), and Polyflon (Daikin) (3)

General Information

Molecular Formula: $(C_2F_4)_n$ (76% F, 24% C)

Structure of Polymer



Uses Teflon is used as an electrical insulator, especially in high frequency applications (1) Electrical uses include coaxial spacers, insulators, wire coating, and tape in electrical and electronic fields (4). Coated glass fibers are also used for conveyor belting, electrical tape, and laminations for electrical uses (3). Teflon may be used to insulate hook-up wire. Films are used to insulate wire and as sheet insulation (5). Other uses include protective clothing (1), gaskets, liners, seals, flexible hose; ablative coatings for rockets and space vehicles; chemical process equipment; aerospace coatings, bearings, seals, piston rings, antistick coatings for cooking vessels and utensils; felts and packing; coating glass fibers for architectural structure composites (4); and filtration fabrics (1).

Thermal Decomposition Mechanisms

Teflon depolymerizes to monomer (CF_2:CF_2), perfluoroisobutylene [$(CF_3)_2C.CF_2$], and carbonyl fluoride (COF_2). The latter hydrolyzes to give CO_2 and HF (6) Thermal degradation proceeds by homolytic statistical chain cleavage (7)

CO_2 and CF_4 result from the disproportionation of COF_2

Hexafluoroethane, CF_3CF_3, and higher perfluoroalkanes apparently form by reaction of COF_2 with the corresponding perfluoroalkenes

The SiF_4 probably arises from reaction of HF with the glass of the infrared gas cell wall or of the gas sampling tube. The hydrogen source is apparently trace moisture (H_2O) (8).

Trifluoroacetic acid, CF_3CO_2H, and HF may form in oxidative pyrolysis from trifluoroacetyl fluoride (9). [Isolated as CF_3CO_2Ca after treating the pyrolyzate with $Ca(OH)_2$ solution.]

The mechanism according to Morisaki (1978) (10) for products having formula $(CF_2)_n$ is as follows

$$R_f\text{-}CF_2\text{-}CF_2\text{-}CF_2\sim\!\!\sim \longrightarrow R_f\text{-}CF_2\cdot + n\ CF_2.$$

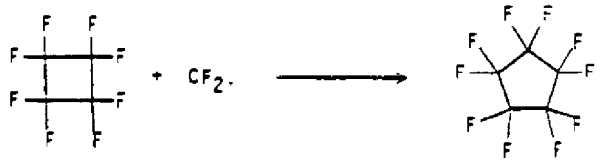
$$2\ CF_2. \longrightarrow CF_2{:}CF_2$$

$$2\ CF_2{:}CF_2 \longrightarrow \text{(cyclobutane)} \longrightarrow CF_3CF{:}CF_2 + CF_2.$$

$$CF_2{:}CF_2 + CF_2{:} \longrightarrow CF_3CF{\cdot}CF_2$$

$$CF_3CF{\cdot}CF_2 + CF_2\cdot \longrightarrow CF_3CF_2CF{\cdot}CF_2 \text{ or } (CF_3)_2C{:}CF_2$$

(and higher homologs) (and higher homologs)



Atkinson and Atkinson (1957, cited by Morisaki, 1978) (10) proposed that C_2F_6 is a decomposition product of perfluoroisobutylene at > 700°C, but stated that such a mechanism cannot be used to produce C_3F_8 or C_4F_{10}

C_4F_6, C_5F_8, and C_6F_{10} may come from decomposition of higher molecular weight fluorocarbons. $C_2F_2H_2$ and C_3F_5H may occur from reaction with contaminant water

COF_2 forms from the reaction of CF_2 and O_2

Summary of Experimental Studies Reviewed

Pyrolysis The monomer tetrafluoroethylene ($CF_2.CF_2$ or C_2F_4) was an intermediate to major product in pyrolyses at atmospheric pressure (7, 9-11)

Major pyrolysis products usually included carbon tetrafluoride (CF_4) (7,10), octafluorocyclobutane (cyclic-C_4F_8) (9,11), and hexafluoropropylene ($CF_3CF.CF_2$ or C_3F_6) (7,9,10). Morisaki (1978) (10) reported numerous other pyrolysis products including octafluoroisobutylene [$(CF_3)_2C:CF_2$] and decafluorobutane (C_4F_{10}) Hydrogen fluoride was seldom reported as a pyrolysis product (2)

At low pressure the monomer was the only important pyrolysis product. Monomer yield in vacuo was highest near 500°C (96.6%) and decreases with increasing temperature (91 20% at 800°C and 78.10% at 1200°C) (12)

Combustion The flash-ignition temperature of Teflon is 560°C, the self-ignition temperature is 580°C (6). CF_4, SiF_4, COF_2, and CO_2 were generally present among combustion products of Teflon and were usually major (9,10,13). Monomer was a major product (60%) from combustion at 700°C (13). Morisaki (1978) (10) found hexafluoropropylene (C_3F_6) to be the most abundant fluorocarbon from combustion at 450 to 790°C. Trifluoroacetyl fluoride (CF_3COF) was reported from combustion at 600 to 650°C (9) Other combustion products reported were octafluoropropane (C_3F_8), octafluoroisobutylene (C_4F_8), and octafluorocyclobutane (C_4F_8) (9,10)

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TEFLON FEP

CASRN. 25067-11-2

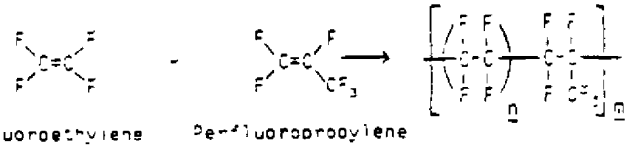
Synonyms Fluorinated ethylene-propylene copolymer, Hexafluoropropylene-tetrafluoroethylene cooolymer

Trade Names (producers): Teflon FEP, Teflon 100 (Du Pont)

General Information

Molecular Formula: $(C_5F_{10})_n$ [Same elemental composition as PTFE. 76% F, 24% C (1)]

Structure of Monomers and Polymer



Tetrafluoroethylene — Perfluoropropylene or Hexafluoropropylene

Uses Teflon FEP is used for plenum signal and fire alarm cable, for insulation for oil well logging cable, and for a wide variety of otner electrical and electronic uses (1) Major electrical uses for Teflon and Teflon FEP have been in military electronics, aircraft, and missiles for their space-saving capabilities Their excellent mechanical and dielectric characteristics allow internal wiring of computers and industrial controls to be miniaturized They are also used in high-frequency cables Fluorinated ethylene-propylene coatings are applied to polyimide film for cable insulation tapes. After winding of the coated film tape on the conductor, the assembly is heated to fuse the lower-melting coating (2)

Thermal Decomposition Mechanisms

Teflon FEP depolymerizes to monomers (3). "Homolytical statistical chain cleavage" gives uncharacteristic fragments. Pyrolysis of branched CF_3 groups gives high yields of perfluoropropylene ($CF_3CF\ CF_2$, C_3F_6) (4). See discussion from reference 8 in preceding subsection on Teflon.

As determined by thermogravimetric analysis coupled with mass spectrometry (TG-MS) in helium, the first-stage degradation gives mainly $CF_3CF{:}CF_2$, which may be liberated directly or evolved via the reaction of $CF_3CF.$ and $CF_2{:}$. C_2F_4 and C_3F_6 evolution at the second stage corresponds to the reactions given in the Teflon discussion Perfluoro-2-butene or perfluoroisobutylene (C_4F_8) may be formed in both stages by the reaction.

$$CF_3CF\ F_2 + CF_2. \longrightarrow CF_2CF_2CF{:}CF_2 \quad \text{or} \quad (CF_3)_2C\ CF_2$$

During pyrolysis, most C_2F_4 is formed at 450 to 550°C by the reaction

$$CF_3CF{:}CF_2 \longrightarrow CF_2\ CF_2 + CF_2$$

Reactions in air include formation of carbonyl fluoride, carbon dioxide, and carbon tetrafluoride:

$$2CF_2 + O_2 \longrightarrow 2COF_2$$

$$2COF_2 \longrightarrow CO_2 + CF_4$$

Summary of Experimental Studies Reviewed

Pyrolysis Major pyrolysis products for Teflon FEP between 400 and 700°C were the monomers $CF_3CF.CF_2$ (C_3F_6) and/or $CF_2\ CF_2$ (there are conflicting reports for results from similar pyrolysis-GC experiments) Other fluorocarbons produced included CF_4, $(CF_3)_2C\ CF_2$ (C_4F_8) or $CF_3CF_2CF{:}CF_2$ (C_4F_8), and perfluorocyclobutane (C_4F_8) [Morisaki (1978) (5) doubted its presence] (3-6) SiF_4 (formed from reaction of HF and glass apparatus with traces of moisture the apparent source of hydrogen atoms), CO, and CO_2 evolved above 650°C (5)

Combustion. Major products in moist air or oxygen were C_3F_6, CF_4, SiF_4, COF_2, CO_2, and trifluoroacetyl fluoride (CF_3COF) (5,6). However, thermogravimetric analysis at ~ 400 to 600°C revealed no SiF_4 and little C_3F_6 and CF_4 Other "combustion" products at 450 to 790°C included octafluoropropane (C_3F_8, $CF_3CF_2CF_3$), decafluorobutane (C_4F_{10}), C_4F_8 (none by TG-MS), and cyclic-C_4F_8 (5)

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2 J. E Hogan. "Wire and Cable Coverings" in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. 13 New York. Interscience Publishers a Division of John Wiley & Sons, 1981, pp. 564-590

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TEFLON PFA

CASRN [Dependent on particular co-monomer used with tetrafluoroethylene]

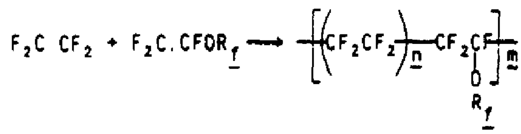
Synonyms Perfluoroalkoxy resin

Trade Names (producers) Teflon PFA (E I du Pont de Nemours). Two melt-viscosity grades TE-9704 and TE-9705 (1).

General Information

Molecular Formula [Dependant on alkyl group]

Structure of Monomers and Polymer:



Uses Teflon PFA is used for injection molded wafer baskets that allow automated production of electronic components in calculators, computers, etc , for valves, fittings, and injection molded complex shapes for components that require the properties of PTFE; and for heat shrinkable and convoluted tubing, roll covers, electric wire insulation, and other electrical industry componants (2) Besides wire and cable insulation, Teflon PFA is used in molded insulating parts such as connector inserts or insulator bushings and standoff insulators. In 1976, developing uses were electrical spaghetti tubing and film for flexible circuits, flat cable, and melt bonding. It is also used for lined valves, pipes, and tanks in chemical processing apparatus and has heat-exchanger applications (1)

Thermal Decomposition Mechanisms

No specific information was found.

Summary of Experimental Studies Reviewed

Only one article (3) was found on thermal decomposition of Teflon PFA, and it had no experimental details. The toxic decomposition product was thought to be partially degraded polymer in particulate form

References

1 R L Johnson "Fluorinated Plastics. Tetrafluoroethylene Copolymers" in Encyclopedia of Polymer Science and Technology Vol Suppl 1 H F Mark and N M Bikales, Editors New York Wiley, 1976, pp 260-278

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TEFZEL

CASRN 25038-71-5

Synonyms: Ethylene-tetrafluoroethylene copolymer, ETFE.

Trade Names (producers): Tefzel (modified ETFE) (Du Pont); Ftorlon 40 (USSR), Hostaflon ET (Hoechst, Germany) T-200 grade is general purpose T-280 for more severe mechanical use.

General Information

Molecular Formula: $(C_4H_4F_4)_n$

Structure of Monomers and Polymer:

$$CH_2{:}CH_2 + CF_2{:}CF_2 \longrightarrow \text{-}(CH_2CH_2CF_2CF_2)\text{-}_n$$

Uses. ETFE is used for high performance wire and cable insulation, back panel wiring in computers, hookup wire for aircraft and mass transit applications (locomotives and cable cars), and wiring in nuclear power plants Injection molded parts of ETFE are used as components in pumps, valves, and other chemical process apparatus; tie wraps; tower packings, and seals and other electronic device components (1) It is specified for wire insulation in U S Navy Mil-W-81822/13, a specification on solderless wrap wire, and in Mil-W-22759/16, /17, /18, and /19, a joint services specification for aircraft wire. ETFE can be applied over bare as well as plated conductors or used as a protective jacket over multiple bundles or coaxial cable (2).

Thermal Decomposition Mechanisms

Tefzel releases minute amounts of HF at processing temperatures of 300 to 320°C It does not undergo an autocatalytic decomposition with elimination of HF at high temperatures. Tefzel undergoes oxidative crosslinking in air above its melting point and undergoes random chain scission above 400°C rather than "unzippering " Its noncharring behavior is typical of a polymer that degrades to low-molecular-weight fractions instead of leaving a residual carbonaceous skeleton by splitting out small molecules (2) Tefzel produces far less smoke under current overload

than do PVC-nylon, poly(vinylidene fluoride)-jacketed polyethylene, or other similar insulations. Two routes are needed to explain the presence of tetrafluoroethylene and vinylidene fluoride ($CF_2:CH_2$) in the decomposition products (3).

$$—CF_2-CF_2-CH_2-CH_2-CF_2-CF_2-CH_2-CH_2— \longrightarrow n\ (CH_2\ CH_2) + m\ CF_2\ CF_2$$

$$—CF_2-CF_2-CH_2-CH_2-CF_2-CF_2-CH_2-CH_2— \longrightarrow CF_2\ CH_2$$

Summary of Experimental Studies Reviewed

Pyrolysis Pyrolysis at 700°C for 10 sec gave three major and several other unidentified products whose retention times on the gas chromatogram were different from those of other fluorinated polymers. The pattern of minor products was typical of that from polyethylene, representing n-alkanes, α-olefins, and α,ω-olefins (4)

Combustion Minor amounts of HF were lost during processing at 300 to 320°C, but 20-hr exposure to 300°C led to ~ 30% weight loss, at 400°C, ~ 40% of the initial weight was lost within 2 hr (5). The only products identified from combustion in the 530 to 580°C range were HF, CO, and COF_2; but some other component was responsible for the toxicity (6) Random chain scission at 650°C for 15 sec gave mostly vinylidene fluoride, $CH_2:CF_2$, with minor amounts of the monomers and HF Alkanes, various C_3 compounds, and higher boiling substances were identified (3,7)

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1 Modern Plastics Encyclopedia. Vol 59, No. 10A. J. Agranoff, Editor New York: McGraw-Hill, Inc., 1982

2 R L Johnson "Fluorinated Plastics. Tetrafluoroethylene Copolymers" in. Encyclopedia of Polymer Science and Technology. Vol. Suppl 1. H. F Mark and N M. Bikales, Editors. New York. Wiley, 1976, pp. 260-278

3 G S Popova, B. I. Sazhin, and N E Shadrina. Study of Products of the Thermal Degradation of a Tetrafluoroethylene-Ethylene Copolymer by the Method of Pyrolytic Gas Chromatography Vysokomol Soedin., Ser B, 21(10), 758-761 (1979).

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VITON

CASRN: 9011-17-0

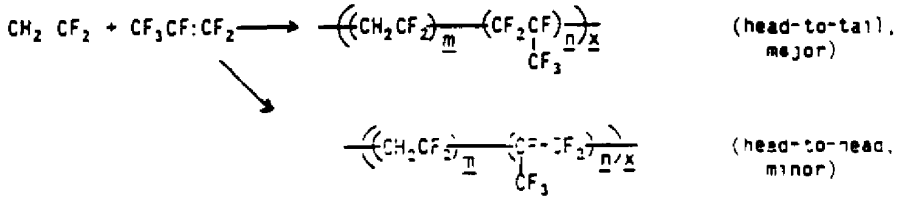
Synonyms. Vinylidene fluoride-hexafluoropropylene copolymer; vinylidene fluoride-hexafluoropropene copolymer.

Trade Names (producers): Viton; Viton A; Viton V (E. I. du Pont de Nemours, Inc.), Refset Fluorel; Fluorel (3M) (no additives); Redar Viton; Viton LM (low-molecular-weight); Dai-El (Daikin), Tecnoflon (Montedison).

General Information

Molecular Formula: [Dependent on relative amounts of the two monomers.]

Structure of Monomers and Polymer:



Uses Viton fluoroelastomers are used in geskets, seals (especially O-rings), tubing, diaphragms, aerospace and automotive components, high vacuum equipment, low-temperature equipment, and radiation equipment (1)

Thermal Decomposition Mechanisms

No specific information was found.

MONS 020457

Summary of Experimental Studies Reviewed

Pyrolysis Pyrolysis at 800°C for 4 sec gave the monomers, trifluoromethane (CHF_3), and hexafluoropropylene-vinylidene fluoride oligomers (2). Pyrolysis at 50 to 460°C gave $CF_3C^+FCH{\cdot}CF_2$ (m/z = 163) and other smaller fragments. The stable product was not identified since the mass spectral "fingerprints" of pyroysis products from other fluorine-containing polymers were simply being compared. Other products included CHF_3, HF, and various oligomers and polymer fragments with weights up to 369 amu (3).

Combustion At 314 to 415°C, the major combustion products identified were CO, CHF_3, and $CH_2.CF_2$ plus fluorinated C_7 to C_8 saturated and unsaturated hydrocarbons (4). Weight loss was 60% after < 1 hr at 400°C. Volatiles were generated at temperatures as low as 200°C (5). At 850°C, combustion gave only CO and CO_2, no HF, F-containing compounds, aldehydes, or carbon aerosols were detected using infrared and gas chromatographic methods (6).

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Section 4

NITROGEN-CONTAINING MATERIALS

CREOSOTE

CASRN. 8001-58-9

Synonyms. Coal tar creosote [to distinguish from beechwood creosote, which is used for medical purposes]; creosote from coal tar, creosote oil [Chemical Abstracts Service assigns this substance a separate registry number]; dead oil; liquid pitch oil; tar oil (1)

Trade Names (Producers). Preserv-o-sote [creosote oil] (Crowley Tar Products Company, Inc.) (2); Nelson's Creosote Wood Preservative (B. F. Nelson Manufacturing Company) (3); Lacco Creosote A.W.P.A. (Los Angeles Chemicals) (3).

General Information

Molecular Formula: Unspecified.

Composition: Coal tar creosote is a high-boiling distillate of coal tar produced by high-temperature carbonization of bituminous coal (4). Residual oils from refining coal tar include heavy naphtha, dephenolated carbolic oil, naphthalene drain oil, wash oil, strained anthracene oil, and heavy oil. These fractions are blended to give "creosotes" or "creosote oils" conforming to specifications such as Standard P1-78 of the American Wood-Preservers' Association (AWPA) (4,5) (see Table 4-1). Timber-preservation creosote is a blend of primarily wash oil or light creosote (boiling range 224-291°C), drained anthracene oil (boiling range 247-355°C), and heavy oil or heavy creosote (boiling range 285-395°C). Besides the creosote defined by AWPA Standard P1-78, AWPA has standards for creosote blended with 20, 30, and 40% coal tar (6,7).

Table 4-1

AMERICAN WOOD-PRESERVERS' ASSOCIATION SPECIFICATION P1-78
FOR TIMBER-TREATING CREOSOTE (4,5)

Fraction Distilling	Components of Fraction	Distillation Range, °C
≤ 2.0%	Unidentified PAHs	< 210
≤ 12 0%		< 235
	Naphthalenes	200-270
10.0-35 0%		< 270
40.0-65.0%		< 315
	Acenaphthene, fluorene, dibenzofuran, phenanthrene, anthracene	270-355
60.0-77.0%		< 355
	Chrysane, fluoranthene, pyrene	> 355

The chemical composition of creosote varies according to the coking temperature and the source of the coal used. Longer carbonization times and higher tamperatures favor PAH formation. Products called creosote that are distilled from sources other than coal are very different in composition from coal tar creosote (6). The remainder of this discussion is restricted to coal tar creosote The word creosote is used unmodified.

Creosote's chemical composition has been characterized by Lijinsky et al (1963) (9), Lorenz and Gjovik (1972) (5), Nestler (1974) (10), and others Table 4-2 lists many of the components, but it is not exhaustive. 162 individual components had been identified by 1952 (10). Creosote contains about 85% polycyclic aromatic hydrocarbons (PAHs), up to 3% tar acids (phenolic compounds), about 5% tar bases (nitrogen-containing compounds), and about 5% benzothiophene and dibenzofuran (S and O analogs, respectively, of the PAH fluorene). Five PAHs--phenanthrene, fluoranthene, fluorene, acenaphthene, and pyrene--account for about 50% of the mass although several other PAHs have been identified and/or quantitated (5,8-13)

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Table 4-2

COMPOSITION OF COAL TAR CREOSOTE

Component	Formula	Concentration, %	Reference
Polycyclic aromatic hydrocarbons (PAHs)		~ 85	10
Phenanthrene	$C_{14}H_{10}$	21.0	5, 10
Fluoranthene	$C_{16}H_{10}$	10.0	5, 10
Fluorene	$C_{13}H_{10}$	10.0	5, 10
Acenaphthene	$C_{12}H_{10}$	9.0	5, 10
Pyrene	$C_{16}H_{10}$	8.5	5, 10
Methylanthracenes	CH_3-$C_{14}H_9$	4.0	5, 10
Chrysene	$C_{18}H_{12}$	3.0	5, 10
Methylfluorenes	CH_3-$C_{13}H_9$	3.0	5, 10
Methylphenanthrenes	CH_3-$C_{14}H_9$	3.0	5, 10
Naphthalene	$C_{10}H_8$	3.0	5, 10
Anthracene	$C_{14}H_{10}$	2.0	5, 10
Benzofluorenes	$C_{17}H_{12}$	2.0	5, 10
Dimethylnaphthalenes	$(CH_3)_2C_{10}H_6$	2.0	5, 10
2-Methylnaphthalene	CH_3-$C_{10}H_7$	1.2	5, 10
1-Methylnaphthalene	CH_3-$C_{10}H_7$	0.9	5, 10
Biphenyl	C_6H_5-C_6H_5	0.8	5, 10
Benz[a]anthracene	$C_{18}H_{12}$	0.3	9
Benzo[a]pyrene	$C_{20}H_{12}$	0.02, 0.3	9, 11
Benzo[j]fluoranthene	$C_{20}H_{12}$	0.03	9
Benzo[k]fluoranthene	$C_{20}H_{12}$	0.02	9
Benzo[e]pyrene	$C_{20}H_{12}$	0.02	9
Benzo[b]chrysene	$C_{22}H_{14}$	0.005	9
Perylene	$C_{20}H_{12}$	0.004	9
Unidentified PAHs	-	< 2	5
Acenaphthylene	$C_{12}H_8$	?	12
Indene	C_9H_8	?	10, 12
PAH analogs containing O & S		~ 5	
Benzothiophene	C_8H_6S		10, 12
Dibenzofuran	$C_{12}H_8O$	5.0	5
Tar bases (N-containing components)		< 5	10
Acridine	$C_{13}H_9N$		10
Aniline	$C_6H_5NH_2$		10
Benzonitrile	C_6H_5CN		10
Carbazole	$C_{12}H_9N$	2.0	5, 10
Indole	C_8H_7N		10
α-Naphthylamine	$C_{10}H_7NH_2$		10
β-Naphthylamine	$C_{10}H_7NH_2$		10
Quinoline	C_9H_7N		10
o-, m-, & p-Toluidine	$CH_3C_6H_4NH_2$		8, 10
Xylidines	$(CH_3)_2C_6H_3NH_2$		8, 10

(continued)

Table 4-2 (continued)

Component	Formula	Concentration, %	Reference
Tar acids (phenolics)		< 3, 10	13, 10
Phenol	C_6H_5OH		6, 10
Cresols	$CH_3C_6H_4OH$		6, 10
Xylenols	$(CH_3)_2C_6H_3OH$		6, 10
Trimethylphenols	$(CH_3)_3C_6H_2OH$		10, 12
3-Ethyl-5-methylphenol	$CH_3(C_2H_5)C_6H_3OH$		10, 12
2,3,5,6-Tetramethylphenol; Durenol	$(CH_3)_4C_6HOH$		10, 12
Naphthols	$C_{10}H_7OH$		6, 10

Uses. Creosote is used for impregnating wood such as railroad ties, utility poles, and marine pilings to protect from rot and worms. In 1978, 34,100,000 gal. creosote, 66,400,000 gal. creosote-coal tar solutions, and 30,200,000 gal. creosote-petroleum were sold for wood-preserving applications. It is also used as a waterproofing agent, a fuel oil constituent, a lubricant for die molds, pitch for roofing, and manufacture of road binders, non-cultural winter wash oils, chemicals, and lampblack (carbon black) (1,7,13,14).

Summary of Experimental Studies Reviewed

Pyrolysis. No specific information was found.

Combustion. Concentrations of PAHs sampled downwind from open burning of creosote-treated railroad ties doused with No. 2 fuel oil were much higher than from similar burning of green wood. The burning produced large quantities of black smoke. The PAHs determined in the total solid particulate (TSP) included acenaphthene, benz[a]anthracene, acenaphthylene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[b]fluoranthene, pyrene, chrysene, benzo[k]fluoranthene, phenanthrene, benzo[g,h,i]perylene, and o-phenylenepyrene (indeno[1,2,3-c,d]pyrene) (listed in approximate order of decreasing yield). Fluorene and naphthalene were detected but not quantitated. Product yields are listed in Table 4-3 (15)

Of the PAHs released by burning, benzo[a]pyrene and dibenz[a,h]anthracene are the strongest carcinogens. Benz[a]anthracene, benzo[k]fluoranthene, chrysene, and o-phenylenepyrene were the other carcinogenic PAHs identified (15) Creosote use has been associated with human skin cancers and is an animal carcinogen, however, creosote-impregnated wood poses little or no danger to humans (1,8)

Table 4-3

PAHs IN AIR TOTAL SOLID PARTICULATES DOWNWIND FROM OPEN BURNING OF CREOSOTE-TREATED RAILROAD TIES DOUSED WITH NO. 2 FUEL OIL (15)

Components	Formula	Concentration in Total[a] Solid Particulate, ppm	Carcinogenic
Acenaphthene	$C_{12}H_{10}$	~ 1380-3380	no
Benz[a]anthracene	$C_{18}H_{12}$	~ 550-1260	yes
Acenaphthylene	$C_{12}H_8$	~ 290-840	no
Benzo[b]fluoranthene	$C_{20}H_{12}$	~ 10-690	yes
Benzo[a]pyrene	$C_{20}H_{12}$	~ 10-690	yes
Dibenz[a,h]anthracene	$C_{22}H_{14}$	~ 10-690	yes
Pyrene	$C_{16}H_{10}$	~ 10-690	no
Chrysene	$C_{18}H_{12}$	~ 50-470	yes
Benzo[k]fluoranthene	$C_{20}H_{12}$	~ 5-230	no
Benzo[g,h,i]perylene	$C_{22}H_{12}$	~ 50-130	no
Phenanthrene	$C_{14}H_{10}$	~ 50-130	no
o-Phenylenepyrene; Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	~ 50-130	yes
Fluorene	$C_{13}H_{10}$	Not quantitated	no
Naphthalene	$C_{10}H_8$	Not quantitated	suspect

[a]Range given for three or four runs based on the ratio of the specific PAH concentration to the concentration of total solid particulates in air

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DICYANDIAMIDE

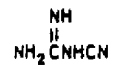
CASRN. 461-58-5

Synonyms Cyanoguanidine, dicyanodiamide, dicy.

General Information

Molecular Formula: $C_2H_4N_4$

Structure:



Paper web is impregnated with dicyandiamide and may (1) or may not (2) be heated (e g , 50°C for 0.5 hr) to dry Heating in air for 15 hr at 135°C may cause some chemical bonding to the cellulose (< 20%) N-containing compounds like dicy "block carbonyl groups and inhibit the chain reaction of oxidation and the thermal destruction of cellulose " Amino groups "block aldehyde groups" (3)

Uses· Dicyandiamide is used in the manufacture of melamine, barbiturates, guanidine derivatives, fertilizers, dyes, explosives, fire-proofing compounds, case-hardening preparations, cleaning compounds, and soldering compounds. It is used as a stabilizer for nitrocellulose and detergent compositions, as a modifier for starch products, and as a catalyst for epoxy resins (4,5).

Paper products produced from lignocellulose pulps are commonly used to insulate various electrical apparatus, e.g., as dielectric spacers in capacitors or insulating sheet for transformer windings. The entire capacitor or transformer winding is typically immersed in a liquid dielectric such as petroleum oil, waxes, or chlorinated hydrocarbons. Various U.S. patents describe methods in which the thermal stability of insulating papers are improved by treating or impregnating with N-containing compounds (such as dicyandiamide or melamine) and/or a protein such as casein or soybean protein (1).

Dicyandiamide is preferred because it is "a particularly good nitrogen-donor to cellulose and therefore a good thermal stabilizer, it is readily available, and it is economical" (1). Optimal concentration of dicyandiamide is 2% based on the weight of the paper (3).

Thermal Decomposition Mechanisms

No information was found.

Summary of Experimental Studies Reviewed

No information was found on the pyrolysis or combustion of paper impregnated with dicyandiamide or on pyrolysis or combustion of dicyandiamide itself

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MONS 020465

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KAPTON

CASRN. 25036-53-7

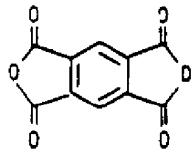
Synonyms. Pyromellitic acid-bis(p-aminophenyl ether) copolymer, polyimide SRU, Poly[(5,7-dihydro-1,3,5,7-tetraoxobenzo[1,2-c 4,5-c']dipyrrole-2,6(1H,3H)-diyl)-1,4-phenyleneoxy-1,4-phenylene] (9CI); Poly[(oxydi-p-phenylene)(pyromellitic diimide)], Benzo[1,2-c:4,5-c']dipyrrole, deriv , polymer (9CI); Bis(4-aminophenyl) ether-pyromellitic anhydride polymer, SRU; 4,4'-Diaminodiphenyl ether-pyromellitic acid copolymer, polyimide SRU; 4,4'-Oxydianiline-pyromellitic anhydride polymer SRU, Poly[N,N'-(oxydi-p-phenylene)pyromellitimide]; Polymer SP; poly[N,N'-(p,p'-oxydiphenylene)pyromellitimide]; Polyimide PM; PM (polyimide).

Trade Names (producers): Kapton, Kapton H (DuPont); Vespel SP-1 (DuPont)

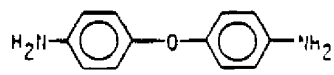
General Information

Molecular Formula: $(C_{22}H_{10}N_2O_5)_n$

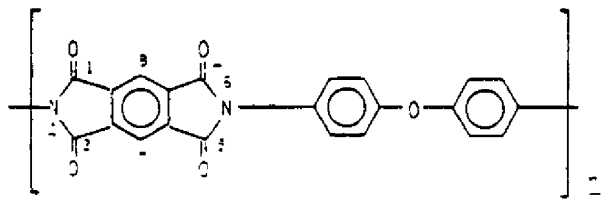
Structure of Monomers and Polymer:



Pyromellitic anhydride



4,4'-Diaminodiphenyl ether



Uses. Thermoset polyimides are advantageous in thin-film products Major applications are those requiring high quality and performance such as the aerospace and electronics markets Electrical applications--Vespel (molded parts) and/or other polyimides such as Kinel (molded parts) and Kerimid 601 (laminates) are used in high-reliability printed wiring boards, integrated circuit carriers as a substitute for ceramics, and automotive parts that require thermal insulation such as wires in electric motors Kapton film is used in electric motors "where size is important " It is used to insulate aircraft and missile wire cable, flat flexible cable, and magnet wire, and used as spaghetti tubing Polyimides may also be used to coat semiconductor devices and electrical components (1)

"DuPont's Vespel SP-1...has been used as an insulating material in molten salt electrochemical power sources which operate at internal temperatures in excess of 400°C" (2)

Thermoplastic polyimides may be used as fibers, film, laminates, or foams Electrical uses include laminates for printed circuit boards. Cast films are being developed for use in flexible printed circuits and insulation for wire cable and electric motors (1).

Thermal Decomposition Mechanisms

Pyrolysis Thermal degradation occurs very drastically in the first few minutes and gradually levels off. Onset of the two stages of pyrolysis depends on the heating rate Most weight loss (~ 40%) occurs during the first stage (below 700°C). The second stage occurs at ~ 900°C and is associated with ~ 4 5% weight loss (3)

First-stage reactions include cleavage of C-N and ether C-O bonds Homolytic cleavage of C-N bonds might be followed by CO elimination and formation of nitrene and benzyne intermadiates (3).

"Uncyclized rings" (that is, monomer units wherein an imide ring did not form and a free carboxyl group is present) may make a "soecial contribution to the degradation reactions of polyimides." There appears to be one uncyclized ring per 8 to 9 polymer units Polyamic acids may denydrate or decarboxylate on heating. Hydrolytic scission with release of CO_2 may occur when water is present. The proposed mechanism does not account for the presence of methane in the products formed from pyrolysis at 700°C Hydrogen may be stripped from aromatic rings at temperatures 600°C (4)

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The following mechanism was proposed to account for the products formed on pyrolysis at 512°C in nitrogen. Loss of CO_2 from the imide carbonyl groups leaves free radical -C.N- linkages, which ultimately leads to bond breaking and formation of free nitriles. Loss of CO from one imide carbonyl group leaves the polymer intact with the remaining amide linkage. Free radical cleavage of the ether linkage of the polymer followed by H atom abstraction gives N-hydroxyphenyl substituted imide molecules (5).

The second stage of pyrolysis may involve formation of a highly conjugated aromatic network from dimerization and trimerization of benzyne intermediates. This network may be responsible for the very stable, electrically conducting material formed by pyrolyzing Kapton [conductivity is 12 $(ohm\text{-}cm)^{-1}$] (3).

A large fraction of the original N content is still present after pyrolysis even at 800°C, therefore, graphitization is minimal (6).

Combustion. No information was found on combustion of Kapton, but its thermal oxidative degradation at ~ 400°C has been studied. Film aged at 400°C in air for a short time undergoes extensive crosslinking during the early stages of oxidation. Crosslinks are too stable to be amide functions. The aryl-ether bond is possibly broken (7).

The major crosslinking reaction apparently occurs through coupling of the diphenyl ether units either by a direct dehydrogenation reaction or by cleavage of the aryl-ether bonds to give phenolic groups that undergo subsequent reactions. The pyromellitimide ring is degraded, forming phthalimide and other ring structures (8).

During oxidation at 400°C, loss of the diphenyl ether units is the fastest process, with 50% of the units having reacted at only 2 to 3% weight loss. This supports the crosslinking mechanism. Within the first 3 hr, ether cleavage, dehydrogenation, and pyromellitimide destruction reactions all proceed at approximately the same rate. After that time, the yield of insoluble polyamines remains about the same, but the yields of soluble aminophenols and modified pyromellitimide units increase up to about 10 hr before leveling off. The polyamines, containing the ether linkage, are probably intermediates in the formation of the aminophenols. Since these reactions are much faster than volatilization loss, the degradation products are from "chemical structures completely different from those of the original polymer." Volatiles come largely from the modified structure (9).

Besides inducing free radical crosslinking, O_2 may react with polymer to give a quinone structure in the aromatic ring attached to the imide N. Further oxidation cleaves that ring to a dicarboxylic acid, heat converts the quinone structure to a char plus carbon monoxide (5).

Summary of Experimental Studies Reviewed

Pyrolysis Most weight loss (~ 40%) occurred below 700°C within the first few minutes of heating [at least at that high a temperature]. A second stage of thermal decomposition began about 900°C but was associated with only ~ 4.5% weight loss (3) Weight loss was low (≤ 5%) after heating for 75 hr at 300 to 350°C but became "catastrophic" (~ 20%) by 400°C within 50 hr (10). Heacock and Berr (1965) (11) reported that Kapton completely disappeared after heating at 500°C [time not given in secondary reference]. The only mechanistic explanation for the source of the major pyrolysis products, CO_2 and CO, was given by Arnold and Borgman (1972) (5), who suggested they came from two imide groups and one imide carbonyl group, respectively. Other inorganic gases formed at 350 to 700°C were hydrogen (H_2), water (H_2O), and hydrogen cyanide (HCN). Benzene (C_6H_6), phenol (C_6H_5OH), and benzonitrile (C_6H_5CN) were reported in this range, too Methane (CH_4) was reported in the volatiles after pyrolysis at 700°C (4). Two reports mention detection of terephthalonitrile (1,4-dicyanobenzene) [$C_6H_4(CN)_2$] at 350-470°C (5) and 600°C (12) Arnold and Borgman (1972) (5) tentatively identified the mass peaks 168-170 as dibenzofuran after pyrolysis at 350 to 470°C. Additional products identified by Hummel et al. (1977) (12) after pyrolysis at 600°C were p-aminophenol ($H_2NC_6H_4OH$), phenyl isocyanate (C_6H_5NCO), phthalimide and five substituted phthalimides, p-aminophenyl phenyl ether ($H_2NC_6H_4OC_6H_5$), three substituted pyromellitimides, and a char. The fact that pyrolysis of Kapton above 700°C gives a highly conductive material suggests that a highly conjugated aromatic network forms, resulting from dimerization and trimerization of benzyne intermediates (3). The char formed from H film pyrolysis at 800°C contained 7% N, 12% O, and 3% H (13).

Combustion. Information on combustion products was not found. Most studies on thermal oxidation of Kapton and other forms of the same polymer focused on the mechanism. After the polymer was heated in air at 300°C for 7 hr, 7.9% of its weight was lost, 95% of the loss was evolved in the first half hour The liquid distillate comprised reaction solvent (dimethylacetamide), polymeric material, and traces of water Gases evolved were CO and CO_2. Part of the oxygen consumed was retained by the polymer (14) Crosslinking accompanied by 50% loss of the diphenyl ether units occurred within 5 hr at 400°C while only 2 to 3% of the polymer's

weight had been lost. At 400°C, the pyromellitimide structure degraded before volatiles were emitted (9)

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NITRILE RUBBER

CASRN 9003-18-3

Synonyms Acrylonitrile-butadiene copolymer; NBR rubber; nitrile-butadiene rubber

Trade Names (producers): Paracril (Uniroyal); Hycar (B. F Goodrich)

General Information

Molecular Formula: $(C_7H_9N)_n$

Structure of Monomers and Polymer:

$$\underset{\text{Acrylonitrile}}{CH_2{:}CHCN} + \underset{\text{Butadiene}}{CH_2{:}CHCH{\cdot}CH_2} \longrightarrow -(CH_2CH{:}CHCH_2CH_2\underset{CN}{CH})_n-$$

Uses: High acrylonitrile content: oil well parts, fuel tank liners, fuel hose, gaskets, packing oil seals, hydraulic equipment. Medium acrylonitrile content: general purpose oil-resistant applications, shoe soles, kitchen mats, sink toppings, printing rolls. Low acrylonitrile content: gaskets, grommets, O-rings (flexible at a very low temparature), adhesives. Binder fuel in solid rocket propellants (1)

Thermal Decomposition Mechanisms

No information was found.

Summary of Experimental Studies Reviewed

Pyrolysis. Major identified products after pyrolysis at 390°C were NH_3 and HCN (each in ~ 5% yield). Traces of hydrogen (H_2), methane (CH_4), and C_1 to C_7 hydrocarbons (mostly C_1 to C_4) were detected in the gases A liquid product (generally produced in ~ 50 to ~ 70% yield) contained unidentified chain fragments. The residue was not characterized (2). The monomers were generally detected after pyrolysis at 500 to 1000°C. Czybulka et al. (1981) (3) who pyrolyzed nitrile rubber at 500°C, gave the most extensive list of other products: HCN; acetonitrile (CH_3CN), propionitrile (CH_3CH_2CN); and C_1 to C_{10} hydrocarbons including toluene ($C_6H_5CH_3$), styrene ($C_6H_5CH{\cdot}CH_2$), ethylbenzene ($C_6H_5C_2H_5$), cyclopentene or pentadiene, and pentane At 590°C, Shimono et al. (1980) (4) found C_1 to C_3 hydrocarbons; butadiene (CH_2 $CHCH{\cdot}CH_2$), acetonitrile (CH_3N), and methacrylonitrile [CH_2 $C(CH_3)CN$] among the pyrolysis products

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Pyrolysis at 610°C of a nitrile rubber containing 33% acrylonitrile (AN) gave the monomers (more butadiene [BD] than AN), AN dimer and trimer, BD dimer and trimer, an AN-BD fragment, and a BD-AN-BD fragment (5). Monomers and vinylcyclohexene, as a minor product, were determined in the products from pyrolysis at 770°C (6)

After pyrolysis at 1000°C, fragments containing one unit of acrylonitrile and one to three units of butadiene predominated over fragments with one to four units of butadiene The monomers were the major products (7).

Combustion No information was found on combustion of nitrile rubber.

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NOMEX

CASRN: 24938-60-1

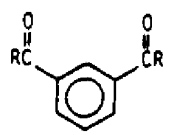
Synonyms Poly(imino-1,3-phenyleneiminocarbonyl-1,3-phenylenecarbonyl), Poly-(imino-m-phenyleneiminoisophthaloyl); Poly(m-isophthalamide), m-Phenylenediamine-isophthalic acid polymer, SRU (structural repeating unit); Isophthaloyl chloride-m-phenylenediamine polymer SRU; Phenylone polymer, Nylon HT

Trade Names: Nomex; Nomex 410, Nomex 450, Aramid KS 305; Aramid KS 105; Conex; Konnekkusu; APH 50.

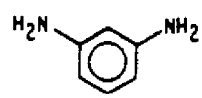
General Information

Molecular Formula: $(C_{14}H_{10}N_2O_2)_n$

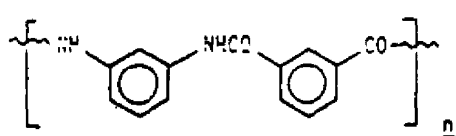
Structure of Monomers and Polymer.



Isophthalic acid (R = OH)
Isophthaloyl chloride (R = Cl)



1,3-Phenylenediamine



Nomex

Uses: Nomex paper, with or without mica flakes, is used to insulate high performance electrical motors, special transformers (e.g., high-voltage dry-type transformers), and aircraft generators. The nonmelting, self-extinguishing Nomex paper is useful up to 180°C. Nomex fibers are also used for aircraft structures, protective garments, and other uses requiring high thermal stability such as filter bags for hot stack gases (1-4).

Thermal Decomposition Mechanisms

Pyrolysis Water loss may occur from chain crosslinking during Nomex pyrolysis at 300 to 400°C. Possible reactions are condensations between terminal amino and carboxyl groups, between chain amide or amino end groups and carboxyl groups, between amide and isoimide groups (tautomeric forms of amide groups), and between two carboxylic acid-terminated chains to give anhydrides. In this temperature range, decarboxylation of end carboxyl groups is the most likely explanation for carbon dioxide evolution (5,6). At least some, if not all, of the water evolved below about 400°C is probably due to water adsorbed by the polymer (6,7)

Products appearing at 400 to 430°C--benzoic acid, 1,3-phenylenediamine, aniline, benzanilide, and N-(3-aminophenyl)benzamide--can be accounted for by heterolytic degradation of chain end and penultimate amide groups and by homolytic amide bond cleavage. Benzonitrile, which is also produced in this range, forms from homolytic cleavage of the aromatic C to amido N bond followed by protonation to give the amide and then dehydration to give the cyano group. [The results of Chatfield et al (6) indicated that the dehydration of amides is the major source of H_2O.] The latter sequence of reactions could also give additional aniline, benzanilide, and N-(3-aminophenyl)benzamide (5). Dehydration of amide groups can also account for formation of 1,3-dicyanobenzene (isophthalonitrile) and 3-cyanobenzoic acid (6). At 475 to 500°C, 1,3-dicyanobenzene is evolved, probably from the same kind of reaction sequence that produces benzonitrile. Larger amounts of water are also evolved (5).

Ehlers et al. (1) proposed a major route for the initial thermal degradation of aramids that involved cleavage of the C-C bond between the aromatic ring and the carbonyl group carbon to give an aromatic isocyanate. Brown and Power (5) considered this mechanism unlikely since no isocyanates were detected in the products. Chatfield et al. (6) did not consider isocyanate formation at all.

The following reactions were proposed by Chatfield et al. (6) for thermal degradation of Nomex (I). [Note: In all formulas, C_6H_4 represents an m-phenylene group.]

$$\underset{(I)}{\text{—NHCOC}_6\text{H}_4\text{CONHC}_6\text{H}_4\text{—}} \xrightarrow[2)\ \text{H atom abstraction}]{1)\ \text{Cleavage}} \underset{(II)}{\text{—NHCOC}_6\text{H}_4\text{CONH}_2} + \text{C}_6\text{H}_4\text{—}$$

$$\text{II} \xrightarrow{\text{Dehydration}} \text{—NHCOC}_6\text{H}_4\text{CN} + \underset{\text{1,3-Dicyanobenzene}}{\text{NCC}_6\text{H}_4\text{CN}} + \text{H}_2\text{O}$$

$$\text{I} + \text{H}_2\text{O} \longrightarrow \underset{\text{III}}{\text{—NHCOC}_6\text{H}_4\text{CO}_2\text{H}} + \text{H}_2\text{NC}_6\text{H}_4\text{—}$$

$$\text{III} \xrightarrow{\text{Decarboxylation}} \underset{\text{IV}}{\text{—NHCOC}_6\text{H}_5} + \text{CO}_2$$

$$\text{III} \xrightarrow[2)\ \text{H atom abstraction}]{1)\ \text{Cleavage}} \underset{\text{3-Cyanobenzoic acid}}{\text{NCC}_6\text{H}_4\text{CO}_2\text{H}}$$

MONS 020474

$$I \xrightarrow{\text{Cleavage}} \cdots NHCOC_6H_4CO^{\cdot} + {}^{\cdot}NHC_6H_4NH\cdots$$
$$\underset{IV}{}$$

$$IV \longrightarrow \cdots NHCOC_6H_4^{\cdot} + CO$$

Combustion. Molecular oxygen apparently reacts extensively with Nomex during thermal degradation in air. For example, at 550°C recovered products contained 42.9% oxygen based on the weight of the original sample, whereas the original sample contained only 12 5% oxygen. CO, CO_2, and H_2O account for most of the oxygen uptake (6).

Summary of Experimental Studies Reviewed

Pyrolysis. Carbon dioxide, water, and carbon monoxide were the major inorganics evolved from Nomex pyrolysis according to most reports. Ehlers et al (7) and Chatfield et al.(6), however, reported that thorough drying of Nomex samples before pyrolysis would preclude water loss during pyrolysis, at least up to 380°C.

Hydrogen and hydrogen cyanide were major inorganics evolved from pyrolysis above 500 or 600°C. Minor inorganics included cyanogen, ammonia, and nitrous oxide (5,7).

Organics usually found in major amounts among the volatile products evolved during pyrolysis below 500°C were benzene, toluene, benzonitrile, 1,3-phenylenediamine, benzoic acid, and aniline. Above 500°C, toluene became a minor product and 1,3-dicyanobenzene became a frequently determined, and often major, product N-(3-Aminophenyl)benzamide and 1,3-phenylenediamine were major products from pyrolysis at 600 and 700°C.

Trace to minor organics reported included C_1 to C_4 alkanes or alkenes, acetylene, nitriles including 3-cyanotoluene (3-tolunitrile), biphenyl and its 3-cyano and 3-amino derivatives, and phenyl isocyanates

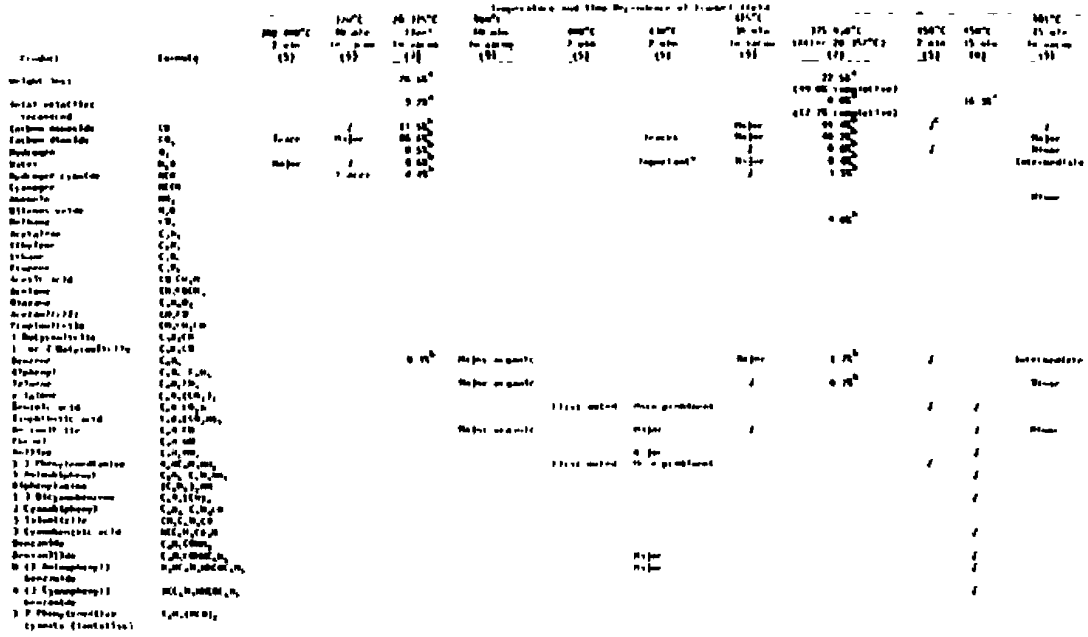
The residue became more aromatic between 450 and 550°C. Loss of most of the hydrogen and oxygen by 1,000°C left a char whose molecular formula approximated $C_{13}NH$ The charred residue comprised about 50% of the original polymer weight after 4 min at 1,000°C under helium (6,8)

Products and their yields for the temperature ranges 300 to 481°C and 500 to 1,000°C are given in Tables 4-4 and 4-5, respectively

Combustion During thermal degradation in air or oxygen, Nomex lost weight rapidly in the range 400 to 600°C and was entirely consumed by 1,000°C (6) Volatile products recovered from degradation at 300 to 1,000°C were primarily water, carbon dioxide, and/or carbon monoxide. HCN at 1.2 weight % (based on the weight of the original sample), acetone at 4.2 weight %, and an unidentified compound of molecular formula $C_{10}H_{12}$ at 7.2 weight % were recovered from flaming combustion and represent the only other products identified in amounts exceeding 1% at any temperature studied. Nitriles, benzene and substituted benzenes, benzoic acid, 3-cyanobenzoic acid, acetaldehyde, acetic acid, alkanes and alkenes, nitromethane, NO, N_2O, and cyanogen comprised most of the remaining combustion products Details are given in Table 4-6

Table 4-4

NOMEX PYROLYSIS BELOW 500°C



[a] Based on weighted polymer weight

[b] Relative to mg 5 based on the total volatiles released.

[c] Products not yet quantified by [illegible]

Table 4-5

NOMEX PYROLYSIS AT 500 TO 1000°C

Product	Isomer	500°C, 2 min (%)	600 °C, (After 20 min.) (%)	600 °C, 2 min (%)	Temperature and Time Dependence of Product Yields: 550°C, 6 min (%)	550°C, 15 min (%)	650°C, 30 sec (%)	650 °C, 2 min (%)	700 °C, 2 min (%)	700 °C, 6 min (%)	1000°C, 4 min (%)	1000°C, 100 min (%)
Weight loss			5.5%[b] from 54 wt%[c]							53.5%[b]	~ 54%[b]	
Total volatiles recovered			3 wt%		80% (27% high boiling; 11% low-boiling)				54% wt%[b]			
Solid residue/char					62%	More dense than at 450°C					~ 97%[b] $C_{1.3}H$	
Carbon monoxide	CO	✓[d]	0.6%	✓	3.2%			✓	Major			
Carbon dioxide	CO_2	✓	2.2%	✓	5.6%			✓	Major			
Hydrogen	H_2	✓	86.5%	✓				✓				
Water	H_2O	✓	0.5%	✓	3.0%			✓	Major			
Hydrogen cyanide	HCN		12.4%		0.04%			Minor	Major			
Cyanogen	$(CN)_2$				Trace							
Ammonia	NH_3											✓
Ethylene oxide	H_2O											
Methane	CH_4		9.1%		0.25%			Minor	Minor			
Bis(methane	CH_2NH_2								Minor			
Acetylene	C_2H_2				Trace				Minor			✓
Ethylene	C_2H_4				Trace			Minor	Minor			
Ethane	C_2H_6				Trace			Minor	Minor			
Propene	C_3H_6				Trace			Minor	Minor			
Butene	C_4H_8								Minor			
Acetic acid	CH_3CO_2H				0.003%							
Acetone	CH_3COCH_3				0.009%							
Diketene	$C_4H_4O_2$				Trace							
Acetonitrile	CH_3CN				0.027%			Minor	Minor			
Acrylonitrile	CH_2CHCN				Trace							
3-Butenitrile	C_3H_5CN				0.013%							
1- or 2-Butenitrile	C_3H_5CN				Trace							
Benzene	C_6H_6	✓	0.06	✓	0.31%			✓	~ 4.0%	✓		✓
Biphenyl	$C_6H_5C_6H_5$							Minor	~ 1%			✓
Toluene	$C_6H_5CH_3$				0.15%			Minor	~ 0%			
m-Xylene	$C_6H_4(CH_3)_2$				0.01%				~ 1.0%			
Benzoic acid	$C_6H_5CO_2H$	✓		✓		Intermediate		✓	~ 0.1 0%			
Anthracene or Pd	$C_{14}H_{10}$ or $C_{16}H_{12}$					Minor						
Benzonitrile	C_6H_5CN	✓		✓	1.3%	Minor	✓	✓	~ 9 1%	✓		✓
Phenol	C_6H_5OH				0.06%	Trace						
Aniline	$C_6H_5NH_2$								~ 7.0%	✓		✓
1,3-Phenylenediamine	$H_2NC_6H_4NH_2$					Major			23.2%			✓
3-Aminobiphenyl	$C_6H_5C_6H_4NH_2$							Minor	~ 1.5%			
Diphenylether	$(C_6H_5)_2O$					Minor						
1,3,5-Triphenylbenzene	$C_6H_3(CH)_3$	✓		✓	0.11%	Major		✓	~ 0%			✓
3-Cyanobiphenyl	$C_6H_5C_6H_4CN$							Minor	~ 0%			
3-Tolunitrile	$CH_3C_6H_4CN$				0.12%			Minor	~ 1%			
3-Cyanobenzoic acid	$NCC_6H_4CO_2H$					Minor						
Benzanilide	$C_6H_5CONHC_6H_5$	✓		✓				Minor	~ 0%			
4-(3-Aminophenyl)-Benzamide	$H_2NC_6H_4NHCOC_6H_5$	✓		✓		Intermediate		Minor	22.2%			

(continued)

Table 4-5 (continued)

Product	Formula	Temperature and Time Regime of Product Yields											
		300°C T min (5)	350 °C (after 30 min) (2)	500-550°C P min (5)	540°C R min[a] (5)	5?0°C P' min (5)	610°C M sec (10)	550-650°C P min (5)	600 or 700°C P min (5)	700 or 800°C R sec (11)	T 800°C + min (5)	3 T 800°C - 100 min (7)
N (1 Cyanophenyl) Benzamide	$NC_6H_4NHCOC_6H_5$											
1 3 Phenylenediiso cyanate (quantified)	$C_6H_4(NCO)_2$											
Phenyl Isocyanate	$NCC_6H_5NH_2$											
Cyanoaniline												

[a] Yields in wt % based on the total volatiles recovered except where noted

[b] Based on original polymer weight

[c] Yields based on peak area of chromatogram except where noted

[d] P - Present but not quantitated here

Table 4-6

NOMEX COMBUSTION

Product	Formula	Isopropanol pyrolysis product yield							
		300°C, 15 min[a] (%)	340-380°C, 15 min[a] (%)	450°C, 5 min[a] (%)	440-520°C, 5 min[a] (%)	550°C, 5 min[a] (%)	600°C, 15 min[a] (%)	800°C, 15 min[a] (%)	Flaming Combustion 30 s, 1 min[a] (%)
Total weight loss		< 1%	< 2.5%	19.5%	< 40%[b]	40%[b]			< 100%
High boiling volatiles						[c]			
Low boiling volatiles						32 (6%)			
Solid residue/char	-	< 99%				60 2%[c]	37%[c]	13.8%[c]	< 0%
Carbon monoxide	CO	0.04%		0.04%		9.5%[c]	17.6%[c]	23.2%[c]	
Carbon dioxide	CO_2	1.1%		1.6 1%		32.8%[c]	42.3%[c]	48.1%[c]	7 1%
Water	H_2O			2.5%		18.3%[c]			15.2%
Hydrogen cyanide	HCN					0.5%[c]	traces[d]	[e]	1 1%
Cyanogen	$(CN)_2$					traces[c]			1 1%
Nitrous oxide	N_2O					0.52%[c]			
Nitric oxide	NO								0 1%
C_1 to C_4 saturated and unsaturated hydrocarbons	-	traces					traces		
Methane	CH_4					traces[f]			
Nitromethane	CH_3NO_2					traces[f]			1 1%
Acetylene	C_2H_2					traces[f]			
Ethylene	C_2H_4								1 1%
Propene	C_3H_6					traces			1 1%
Methanol	CH_3OH								1 1%
Acetaldehyde	CH_3CHO								0 0.1%
Acetic acid	CH_3CO_2H					traces[c]			1 1%
Acetone	CH_3COCH_3					traces[c]			1 1%
Diazene	$C_2H_2N_2$					traces[c]			
Acetonitrile	CH_3CN			0 1%		traces[c]			
Acrylonitrile	CH_2CHCN					traces[c]			
2-Butenenitrile	C_3H_5CN					traces[c]			
1- or 2-Butenenitrile	C_3H_5CN					traces[c]			
Benzene	C_6H_6			0 1%		traces[c]	0 7%[c]	[e]	1 1%
Toluene	$C_6H_5CH_3$			0 1%		traces[c]	traces[c]	[e]	1 1%
m-Xylene	$C_6H_4(CH_3)_2$			0 0%		traces[c]			1 1%
Styrene	$C_6H_5CH=CH_2$								1 1%
Methylstyrene (o-, m- or p-isomer)	$C_6H_4C_3H_5$								1 1%[c]
Unidentified	C_nH_{2n}								1 1%
Unidentified	C_nH_{2n-2}								1 1%
Unidentified	C_nH_{2n-6}								1 1%
Phenol	C_6H_5OH					traces[c]			
Benzoic acid	$C_6H_5CO_2H$					traces[c]			
Benzonitrile	C_6H_5CN			0 1%		0 1%[c]	0 0%[c]	[e]	1 1%
1,3-Dicyanobenzene	$C_6H_4(CN)_2$					traces[c]			
Isophthalic	$CO_2H_2C_6H_4$			0 1%		traces[c]			
3-Cyanobenzoic acid	$HC_6H_4CO_2H$					[f]			

[a] Based on original polymer weight

[b] Based on mass lost at total volatiles collected

[c] Mass less than 1 weight %

[d] Present but not quantified here

[e] 0.1% of 1%

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MONS 020481

NYLON 6

CASRN: 25038-54-4

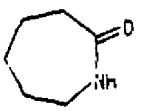
Synonyms. Poly(iminocarbonylpentamethylene); polycaprolactam; polycaproamide, caprolactam polymer

Trade Names (producers). Capron (Allied Corp); Fosta (American Hoechst), Ultramid (Badische Corp.), CRI (Bemis Co.), Firestone (Firestone), Enkalon, Grilon (Emser Werke), Mirlon; Perlon, Phrilon; Amilan (Toray Ind., Inc.).

General Information

Molecular Formula: $(C_6H_{11}NO)_n$

Structure of Monomer and Polymer:



ε-Caprolactam

$-\{NHCO(CH_2)_5\}_n$

Nylon 6

Uses. Nylon 6 is used in bearings, gears, bushings, coil forms, brush backs, tubing, and tape (1). It is widely used in meat packaging (2) Nylon plastics are used in numerous consumer products, including tire cord, fishing lines, tow ropes, garden hose, and woven fabrics (3). In general, nylons have their biggest markets in the automotive industry for applications such as electrical connectors wire jackets, emission cannisters, and light-duty gears Electrical and electronic applications use large amounts of nylons. Fire retardant (UL94 V-0) nylons are used in the electronic and electrical fields. Nylons are used for plugs, connectors, wire devices, terminals, cable ties, wire jacketing, antenna mounting devices, and power tool housings (2). In wire and cable applications, nylons are used as jacketing underwhich the primary insulation is polyethylene or poly(vinyl chloride) (4).

Thermal Decomposition Mechanisms

Based on mass spectral data, water elimination (-18 amu), loss of the acid amide group (-44 amu) after rearrangement, and loss of methylene groups from longer polyamides (-42 or -56 amu) by cis-elimination form most of the decomposition products

Polyamides and copolyamides with a large number of methylene groups favor decomposition by cis-elimination and cleavage of the amide bonds (5) Nylons apparently degrade initially by random chain scissions of bonds between N and carbonyl-group C (the weakest link), between N and methylene-group C beta to a carbonyl group (the second weakest link), and between C's of adjacent methylene groups beta to a carbonyl group In addition, hydrolysis produces amines and carboxylic acids Decarboxylation of the latter is the source of most of the CO_2 evolved. Nitriles arise from dehydration of amides (6)

Summary of Experimental Studies Reviewed

Pyrolysis Recent reviews list thermal decomposition products of polyamides as carbonaceous residue and volatile products such as NH_3, nitriles, amines, cyclic ketones, esters, CO, CO_2, H_2O, hexamethyleneimine (hexahydro-1H-azepine), hexylamine, heptylamine, and methylamine (7,8).

Ohtani et al (1982) (9) generalized about the kinds of products generated from pyrolysis of various nylons at 550°C. The major differences were that cyclopentanone is a prevalent degradation product if adipic acid was one of the starting materials and that those mononitriles formed that contain one amide group have different structures depending on the starting materials If the nylon has been manufactured from an ω-aminocarboxylic acid, the mononitrile with one amide group has the CN group in the N-alkyl portion of the molecule (I and II)

$$CH_3(CH_2)_m CONH(CH_2)_n CN \qquad (I)$$

$$CH_2{:}CH(CH_2)_{m-1} CONH(CH_2)_n CN \qquad (II)$$

If the nylon is a condensation product of a diamine and a dicarboxylic acid, the mononitrile with one amide group has the CN groups in the carboxylic acid group of the amide (III and IV).

$$CH_3(CH_2)_m NHCO(CH_2)_n CN \qquad (III)$$

$$CH_2{\cdot}CH(CH_2)_{m-1} NHCO(CH_2)_n CN \qquad (IV)$$

Other products of nylon pyrolysis include saturated hydrocarbons, α-olefins (which give the strongest intensities of the hydrocarbons), ω-dienes, mononitriles with either a saturated carbon chain or an ω-olefin chain, lactams, dinitriles, and

hydrocarbons with one amide group with an ω-double bond in the carboxyl group and with or without an ω-double bond in the alkyl substituent (9)

Pyrolysis of nylon 6 (polycaprolactam) at 530°C gave a strong peak for caprolactam and lesser peaks for C_6 mononitriles and for mononitriles with one amide group (9)

Other studies report nylon 6 pyrolysis products that include caprolactam dimers, trimers, tetramers, etc (10,11) [at 30 to 400°C] Bahr et al. (1984) (5) found oligomers containing up to 16 repeating units (M) in the pyrolysis products from nylon 6 degraded at 50 to 600°C Most products took the forms $[M_{3-15} + Na]^+$, $[M_n + K]^+$, and $[M_n + H]^+$. The most abundant $[M_n + Na]^+$ had n = 5 to 7 For $[M_n - Na - H_2O]^+$, the most abundant species had n = 8 or 9.

Combustion No specific information was found on nylon 6 combustion products The flash-ignition temperature of nylon 6 is 420°C, the self-ignition temperature is 450°C (7)

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6 H. H G. Jellinek and S. R. Dunkle. "Hydrocyanic Acid Evolution from Polyamides, Polyurethanes, and Polyimides and a Survey of Their Thermal and Oxidative Degradation" in. Degradation and Stabilization of Polymers Vol 1 H H G. Jellinek, Editor. Amsterdam, Neth Elsevier, 1983, pp 66-161

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10 R E. Adams. Positive and Negative Chemical Ionization Pyrolysis Mass Spectrometry of Polymers. Anal Chem, 55, 414-416 (1983)

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NYLON 6,6

CASRN: 32131-17-2

Synonyms Poly(hexamethylene adipamide); hexamethylenediamine-adipic acid copolymer; poly(iminocarbonylbutylenecarbonyliminohexamethylene)

Trade Names (producers). Celanese (Celanese Corp.); Zytel (DuPont), Vydyne (Monsanto), Maranyl (Imperial Chemical Industries).

General Information

Molecular Formula: $(C_{12}H_{22}N_2O_2)_n$

Structure of Monomers and Polymer:

$H_2N(CH_2)_6NH_2$ Hexamethylenediamine

$HO_2C(CH_2)_4CO_2H$ Adipic acid

$$-\left[NHC(CH_2)_4\overset{O}{\overset{\|}{C}}NH(CH_2)_6\right]_n$$

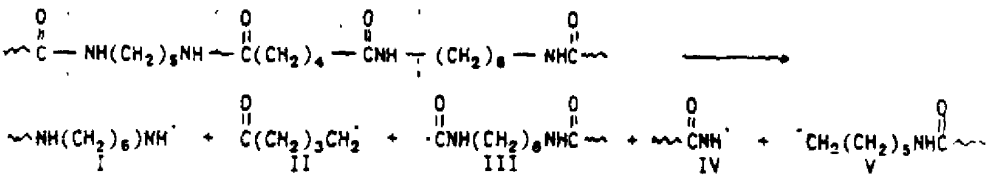
Uses Nylon 6,6 is used for bearings, gears, bushings, coil forms, brush backs, rod, and tubing (1).

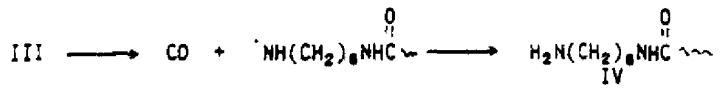
Thermal Decomposition Mechanisms

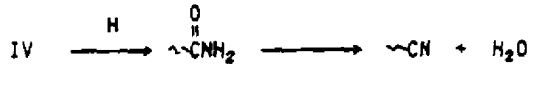
General information for nylons is discussed under nylon 6, above Cyclopentanone may be produced after chain scission of the carbonyl-nitrogen and methylene-carbonyl links give the requisite 5-carbon precursor or from cleavage of an end-group adipic acid followed by decarboxylation and cyclization Hydrolysis generates some of the products At lower temperatures, chain scission predominates, with production of cyclopentanone and CO Temperatures around 600°C produce

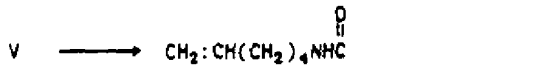
cyclohexane, olefins, and fragments with intact amide groups (all fragments with m/e ≥ 140). Jellinek and Dunkle (2) presented the following scheme for thermal degradation of nylon 6,6:

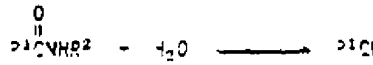
Lower temperatures:

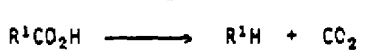




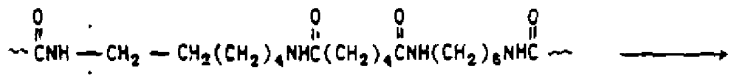


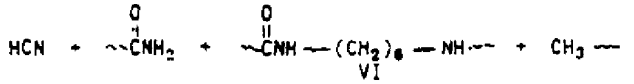


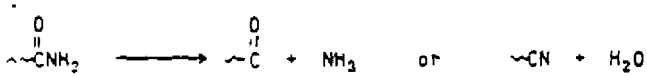


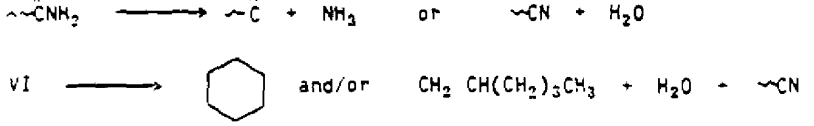


Higher temperatures (> 600°C):









Summary of Experimental Studies Reviewed

Pyrolysis. Ohtani et al. (1982) (3) found cyclopentanone as the major nylon 6,6 pyrolysis product at 550°C Minor products include caprolactam and a C_6 dinitrile Bahr et al. (1984) (4) pyrolyzed nylon 6,6 at 50 to 600°C, identifying peaks corresponding to $[M_{2-s} + H]^+$, $[M_{2-s} + Na]^+$, $[M_2 + 2Na]^{2+}$, and a very weak $[M_n + Na - H_2O]^+$ Main fragments corresponded to $[M_n + Na - 44]^+$, $[M_n + Na - 84]^+$, and $[M_n + Na - 110]^+$ where 44 is a loss of $CONH_2$, 84 is a loss of $(CH_2)_4CO$, and 110 is a loss of $(CH_2)_4CO$ and CN. After Burns and Renschler (1984) (5) pyrolyzed nylon 6,6 yarn at 500°C, they identified major products as cyclopentanone, adiponitrile (tentatively), and a "composite of caprolactam and an apparent homolog "

Adams (1983) (6) reported the presence of the following mass spectral peaks (abundance relative to cyclopentanone as 100%) after nylon 6,6 pyrolysis at 30 to 400°C 143 (16%), 183 (15%), 227 (15%) (227 is the weight of the repeating unit), 343 (47%), 369 (31%), and 409 (25%). Except for the common occurrence of cyclopentanone, there was little agreement among the references as to the products formed (all three reports identified them by mass spectral analysis)

Combustion Jellinek and Dunkle (1983) (2) studied the evolution of HCN from nylon 6,6 films during flash degradation at 289 to 695°C in air. The amount of HCN evolved reached a maximum of ~ 14% of theoretical at ~ 500°C within 16 min. At 695°C, HCN evolution was much less than 1% of theoretical because of its oxidation, which began at ~ 575°C.

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3 H Ohtani, T. Nagaya, Y. Sugimura, and S Tsuge. Studies on the Thermal Degradation of Aliphatic Polyamides by Pyrolysis-Glass Capillary Gas Chromatography. J. Anal Appl Pyrolysis, 4(2), 117-131 (1982)

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MONS 020487

6. R. E. Adams. Positive and Negative Chemical Ionization Pyrolysis Mass Spectrometry of Polymers. Anal Chem., 55, 414-416 (1983).

NYLON 6,10

CASRN 9008-66-6

Synonyms: Hexamethylenediamine-sebacic acid copolymer

Trade Names (producers). Tynex

General Information

Molecular Formula. $(C_{16}H_{30}N_2O_2)_n$

Structure of Monomers and Polymer:

$H_2N(CH_2)_6NH_2$ Hexamethylenediamine

$HO_2C(CH_2)_8CO_2H$ Sebacic acid

$$-\left[NHCO(CH_2)_8CONH(CH_2)_6\right]_n-$$

Uses: Jacketing for wire and cable, special molded parts (1).

Thermal Decomposition Mechanisms

No specific information was found for nylon 6,10.

Summary of Experimental Studies Reviewed

Pyrolysis. Ohtani et al. (1982) (2) found the following compounds in the products from pyrolysis of nylon 6,10 at 550°C. caprolactam, C_6 to C_8 hydrocarbons (C_6 major), C_6 to C_8 mononitriles (C_6 major), 1,10-decanedinitrile, and C_{14} to C_{16} mononitriles with one amide group (C_{16} major)

Combustion. No specific information was found.

References

1 J. E. Hauck, Editor 1974 Materials Selector Vol. 78(4) Stamford, Conn Reinhold Publishing Company, 1973

MONS 020488

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NYLON 11

CASRN· 25038-74-8

Synonyms. Poly(ω-undecanamide)

Trade Names (producers): Rilsan (Rilsan Corp.)

General Information

Molecular Formula. $(C_{11}H_{21}NO)_n$

Structure of Monomers and Polymer:

$H_2N(CH_2)_{10}CO_2H$ — ω-Aminoundecanoic acid

$-[NHCO(CH_2)_{10}]_n-$ — Nylon 11

Uses: Electricel insulation and other nylon uses where low moisture absorption is needed (1). Mainly used for pressure moldings and fibers (2).

Thermal Decomposition Mechanisms

No specific information was found for nylon 11

Summary of Experimental Studies Reviewed

Pyrolysis Ohtani et al. (1982) (3) pyrolyzed nylon 11 at 550°C The lactam produced from undecanamide geve the weekest peak. Other weak peaks were ascribed to C_{14} to C_{20} mononitriles with one emide group and C_3 to C_{21} hydrocarbons with one amide group Intermediate-to-strong peaks were ascribed to C_8 to C_{11} mononitriles with the C_{11} species predominant. C_6 and C_7 hydrocarbons were the most abundant of all species identified. C_2 to C_{10} hydrocarbons were present in intermediate abundance

Combustion No specific information was found

MONS 020489

References

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2 R E Putscher. "Polyamides" in: Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 18. M. Greyson, Editor. New York: Interscience Publishers, a Division of John Wiley and Sons, 1982, pp. 328-371.

3 H. Ohtani, T. Nagaya, Y Sugimura, and S. Tsuge. Studies on the Thermal Degradation of Aliphatic Polyamides by Pyrolysis-Glass Capillary Gas Chromatography. J Anal. Appl. Pyrolysis, 4(2), 117-131 (1982).

POLYURETHANES

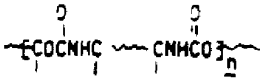
CASRN. Dependent on monomers

Synonyms Urethane polymers

General Information

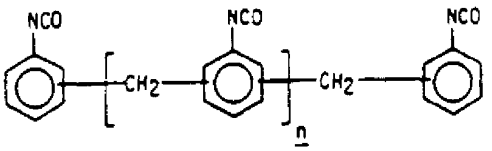
Molecular Formula: Variable

Structure of Monomers and Polymer: Polyurethanes contain the carbamate or urethane group -NHCOO- and are produced by reacting diisocyanates, e.g., toluene-2,4-diisocyanate [$CH_3C_6H_3(NCO)_2$], with a so-called polyol or macroglycol based on polyethers and/or polyesters or with a combination of macroglycol and a short-chain glycol extender. Linear, thermoplastic polyurethanes may have the general structure:



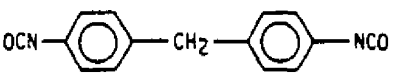
Crosslinked thermoset polyurethanes are prepared from isocyanates and polyols of functionality > 2. Crosslinking can also occur from secondary reactions to give urea linkages [-NHCONH-] and biuret linkages [-NHCON(CONH-)-]. The latter reactions are common in water-blown polyurethanes (evolving CO_2 acts as a blowing agent) (1).

Rigid foams are derived primarily from polymethylene polyphenyl isocyanate (PMDI), often linked with polyester polyols Rigid foam from PMDI is preferred for commercial refrigeration insulation, but household refrigerators use a rigid foam based on toluene diisocyanate (TDI).



PMDI

PMDIs are crude products containing 40 to 60% 4,4'-methylenebis(phenyl isocyanate) (MDI) Pure MDI is used in elastomers.



MDI

Flexible foams are primarily based on polyether polyols. TDI, PMDI, or PMDI-TDI blends are often used as the isocyanate

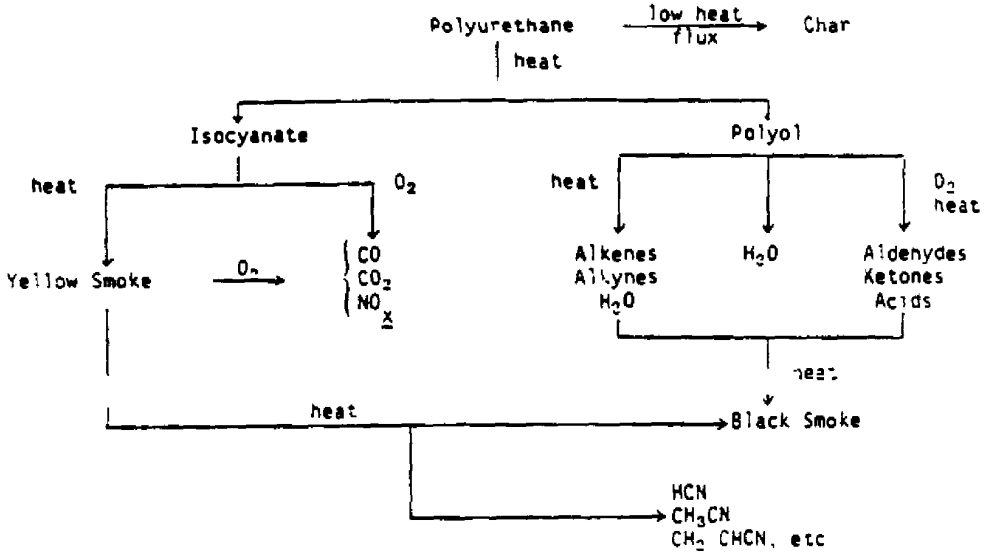
About 50% of polyurethane coatings are based on TDI with polyethers or polyesters Polyurethane alkyds, moisture-cured polyurethanes, and self-crosslinking aqueous polyurethane dispersions are other coating types (1).

Uses: Flexible polyurethane foams are used in furniture, transportation, bedding, carpet underlay, textile laminates, and packaging (listed here in order of decreasing U.S consumption in 1981) Rigid foams are used in building and construction, refrigeration, tank and pipe insulation, transportation, packaging, and furniture (1). Polyurethanes are used to enamel magnet wire that will be used in soldering applications Polyurethanes may also be used to replace oil-modified alkyds used in electrical equipment to bond windings for improved vibration resistance Although several other synthetic resins are available for the purpose, polyurethanes or epoxies are chosen when chemical resistance is important (2) Polyurethane foam is among the materials that have been proposed as insulation for cryogenic resistive cable pipe (A cryogenic resistive cable is an insulated conductor cooled to reduce the electrical resistivity of the conductor Cables are cooled to cryogenic temperatures, typically that of liquid nitrogen) The feasibility of using polyurethane foam to insulate air-cooled underground transmission lines has also been studied (3) A European reference (4) listed polyurethane among commercially available organic cable insulation and jacket materials

Thermal Decomposition Mechanisms

Three pathways were proposed by Saunders (1959; cited by Hileman et al , 1975) (5) (a) dissociation to the original polyol and isocyanate; (b) cleavage by a concerted reaction, producing a carbamic acid (which further decomposes to an amine and CO_2) and an olefin from the polyol; and (c) loss of CO_2 probably accompanied by intramolecular recombination of the olefin and primary amine to give a secondary amine When Hileman et al. (1975) (5) pyrolyzed a polyol-TDI polyurethane, only pathway (a) appeared to be operative below 300°C. Pathways (a) and (b) were operative above 300°C plus other secondary decompositions Lack of volatile secondary or tertiary amines seemed to indicate that if pathway (c) were operative, it occurred without polymer chain cleavage.

Grayson et al. (1982) (6) proposed the following scheme for combustion of polyurethane foams:



Summary of Experimental Studies Reviewed

All the information found was on flexible polyurethane foams, mostly based on TDI and polyether polyols

Pyrolysis. At 300°C, flexible polyurethane foams based on TDI and a polyether polyol evolved a yellow smoke containing all of the nitrogen from the polymer About 30% of the original polymer weight is lost (7) The yellow smoke, which was stable up to ~ 800°C, appeared to contain compounds with polyether linkages, isocyanate groups, and possibly ureido linkages and amino groups (8). CO was also evolved at 300°C with a two-step pyrolysis at 300°C, then 1000°C, giving less CO than if the polymer was heated in one step at 1000°C (7). The major volatile products (other than the yellow smoke) observed by Hileman et al. (1975) (5) when a polyurethane was pyrolyzed at 300°C were H_2O, propene ($CH_3CH{:}CH_2$), and CO_2 (in order of increasing amounts). At 500°C, CO_2, acetaldehyde (CH_3CHO), propionaldehyde (CH_3CH_2CHO), and propene were found (in order of increasing amounts). At 750°C, which was still below the temperature at which the yellow smoke decomposed, the products found (in order of increasing amounts) were lower alcohols (CH_3OH and CH_3CH_2OH), CO, CO_2, CH_4, H_2O, C_1 to C_3 saturated and unsaturated hydrocarbons, acetaldehyde, and propionaldehyde (5).

Pyrolysis at 800 to 1000°C gave HCN, benzonitrile, acetonitrile, pyridine, and acrylonitrile to be major products (7-9). Other products included C_2 to C_4 saturated and unsaturated hydrocarbons; other C_2 and C_3 nitriles and cyanotoluene; the aromatic hydrocarbons benzene, toluene, styrene or cyclooctatetraene, naphthalene, and indene; and the heterocyclic aromatic compounds pyrrole, methylpyridine, vinylpyridine, and quinoline or isoquinoline (7,9).

Propionaldehyde, propene, and acetaldehyde were the major products found by Hileman et al. (1975) (5) after ~ 30% weight loss from pyrolysis at 1000°C. They also found more of the other products detected at 750°C. Presumably, decomposition at 1000°C was the source of the nitrogenous products reported. TDI, toluenediamine, dicyanobenzene, benzonitrile, and other nitriles. Other pyrolysis products were toluene, benzene, styrene, xylene, alcohols, ether alcohols, ethers, and acetone (yields were not calculated although labeled chromatograms are given in the reference)

About 50 products from pyrolysis of rigid polyurethane foams were identified in a 1986 review (10).

Combustion During full-scale combustion of a polyol-TDI polyurethane, the temperature attained at least 1000°C within a few minutes Hydrogen cyanide (HCN) yields reached a maximum of 0.6% and represented a toxic hazard comparable to that

of the CO generatad within the first 5 min. After that time, HCN yields declined, possibly due to a rapid loss of yellow smoke, leaving the polyol residues. The CO concentration (total ~ 8%) remained steady from ~ 5 to 20 min of burning (7)

Boettner et al (1973) (11) reported that combustion losses of CO_2 and CO were higher than those of propene, HCN, and aldehydes. Yields of acetone, hydrocarbons, and methanol were even lower. Woolley (1973) (7) remarked that the same products (HCN, nitriles, N-containing heterocycles, and lower and aromatic hydrocarbons) were formed from combustion as from pyrolysis, but that they were formed at lower temperatures during combustion.

About 90 combustion products from rigid polyurethane foam were identified in a recent review (10).

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MONS 020494

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MONS 020495

Section 5

SULFUR-CONTAINING MATERIALS

See also creosote in Section 4, Nitrogen-Containing Materials.

CHLOROSULFONATED POLYETHYLENE

CASRN 9008-08-6

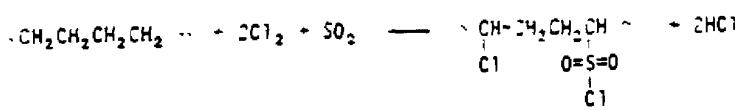
Synonyms Rubber, synthetic, chlorosulfonated polyethylene; Chlorosulfonated polyethylene synthetic rubber; CSPE.

Trade Names (producers): Hypalon; Hypalon 40 (E. I. du Pont de Nemours, Inc.), Colladex

General Information

Molecular Formula: Best rubber properties: 30 to 35% Cl and 0.8 to 1.5% sulfonyl sulfur.

Structure of Starting Materials and Polymer:



CSPE may be crosslinked by use of PbO, MgO, or tribasic lead maleate with a sulfur-containing accelerator, usually dipentamethylenethiuram tetrasulfide It can also be cured with epoxy resins. A crosslinked polymer useful for wire coverings for bare copper or use with lead in hose and cables can be prepared by the use of metal oxides or hydroxides, rosin acids, and a free-radical scavenger such as a nitrosamine, nitrosohydroxylamine, or hindered phenol (1)

Uses Electrical uses include wire and cable (appliance cords, ignition wire, telephone handset cords, and weatherproof wire) An important use is for flexible,

decorative, and protective coatings for fabric, metal, rubber, masonry, and other surfaces (1).

Chlorosulfonated polyethylene is preferred over neoprene for jacketing of insulating cables for fixed installations. The CSPE jacket replaces part of the conductor insulation. When color coding is desired for open-pit, portable mining cables, pigmented CSPE jackets are used (2). Hypalon is now widely specified for sheathing oil-drilling platform cables instead of poly(vinyl chloride) (3).

Other uses include weather stripping and automobile window channels; leather-like coated fabrics, floor tile; automotive products such as distributor caps, sparkplug covers, and ignition wire jacketing, hoses for steam, water, and corrosive chemicals, chemical tank linings, surfacing of conveyor belts, gaskets or diaphragms requiring resistance to ozone, the weather, heat, or oils, and adhesives (1).

Thermal Decomposition Mechanisms

SO_2Cl groups are lost followed by dehydrochlorination to form a polyene. Crosslinking may occur by intermolecular elimination of HCl and/or a Diels-Alder type reaction between two dehydrochlorinated polymer molecules. Thermal degradation then proceeds principally by 1:5 hydrogen transfer. This gives C_3- to C_6 1-alkenes. Limited unzipping gives C_2H_4. Secondary pyrolysis occurs above 627°C. Higher 1-alkenes formed during primary pyrolysis are degraded to lower-molecular-weight products probably by dissociation of free radicals and intramolecular cyclic dissociation. Above 727°C, further fragmentation, cyclization, and aromatization occur; hydrogen yields increase, C_2 and C_4 products decrease. CH_4 production maximizes at ~ 827°C, toluene yields decrease above 827°C, benzene yields plateau in the range ~ 700 to 1100°C; naphthalene yields reach their maxima about 847°C, and, finally, only small fragmentation products and large polynuclear aromatics are present (4).

Summary of Experimental Studies Reviewed

Pyrolysis. At pyrolysis temperatures < 627°C, major products include C_3 to C_5 1-alkenes and HCl. For example, major products at 497°C were reported as ethene and ethane, propene and propane, 1-butene, 1,3-butadiene, and toluene, at 597°C propene and propane, ethene and ethane, benzene, and toluene. Above 627°C, the 1-alkenes break down to lower fragments, thus, CH_4 appears as a major product. Above 727°C, cyclization and aromatization products are largely predominant.

However, the C_2 (ethane and ethene) maximum is ~ 827°C. At 927°C, large polycyclic aromatic hydrocarbons are among products with high yields of benzene and naphthalene (4). The large polycyclic aromatic hydrocarbons detected were acenaphthene, fluorene, anthracene, and phenanthrene. Other products were styrene, toluene, indene, 2- and 1-methylnaphthalene, biphenyl, and dimethylnaphthalene

Combustion. No information was found on organics in combustion products. Combustion of chlorosulfonated polyethylene (CSP) cable sheath material compounded for reduced acid ges emission gave concentrations of the products in the order CO_2 > CO > HCl > SO_2. A standard type of CSP cable sheath material that had not been compounded for reduced acid gas emission gave products with concentrations in the order CO_2 > HCl > CO > SO_2 (3).

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POLYSULFONE

CAS RN 25135-51-7

Synonyms: Bisphenol A - 4,4'-dichlorodiphenyl sulfone copolymer

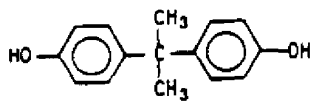
Trade Names (producers): Udel (Union Carbide)

General Information

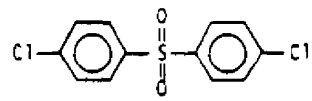
Molecular Formula: $(C_{27}H_{22}SO_4)_n$

MONS 020498

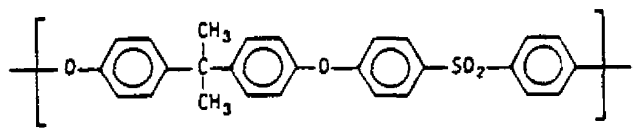
Structure of Monomers and Polymer



Bisphenol A



4,4'-Dichlorodiphenyl sulfone



Polysulfone

Uses Electrical/electronic applications include connectors, auto fuses and switches, housing, coil bobbins and cores, TV components, capacitor film, and structural circuit boards. In chemical processing equipment, polysulfone is used for corrosion resistant piping, both transparent and glass fiber bonded; for tower packing; and for pumps, filter modules and support plates, and membranes. Polysulfone is also used for camera and watch cases, battery cell frames and housings, auto and aerospace components, water purification devices, medical instrumentation and trays to hold instruments during sterilization, and food processing equipment (1).

Thermal Decomposition Mechanisms

During thermal and thermooxidative degredation of polysulfone, crosslinking and chain-scission reactions are caused principally by reactions of free radicals with the aromatic nuclei. Iron and diphenylolpropane (DPP) impurities affect the course of thermal degradation of polysulfone. Both iron and DPP accelerate oxidation of aliphatic groups and thermal decomposition. Thermal degradation products of DPP destroy or retard crosslinking, reacting with the polymers as low-molecular-weight radicals. Iron impurities accelerate crosslinking (2).

Summary of Experimental Studies Reviewed

Pyrolysis. Pyrolysis at 460 to 520°C caused a 62% weight loss of the polysulfone sample (3) Radiant pyrolysis of a sample containing up to 1% carbon black for 2 min at 4 cal cm^{-2} sec^{-1} left 31% char (4,5) No chemical products were identified

Combustion Thermal oxidation at 350°C for 80 hr caused less than 10% weight loss In the same period, ~ 70% was lost at 400°C (6) Combustion for ~ 0 5 hr at 400°C produced little smoke, and the combustion products caused little sensory irritation in mice (7). Combustion of polysulfone at < 450 to 750°C in an atmosphere somewhat deficient in oxygen gave primarily CO_2, CO, SO_2, and a residue. The next most abundant volatiles were methane (CH_4), benzene (C_6H_6), and toluene ($C_6H_5CH_3$) Minor amounts of ethylene (CH_2 CH_2), ethane (C_2H_6), ethylbenzene ($C_6H_5C_2H_5$), and styrene (C_6H_5CH CH_2) were determined. Measured products accounted for 92.6% of the sulfur content but only 60% of the total mass (3).

About half of the weight loss from polysulfone combustion was a liquid residue Some carbonyl sulfide (COS) was detected in the gases after combustion at 490 to 550°C, the range where SO_2 evolution was greatest Phenol and phenyl p-tolyl ether were the major combustion products at 1000°C. Hydrocarbon products included toluene, ethylbenzene (or xylene), styrene, methylethylbenzene, indene, methylindene, trimethylbenzene, naphthalene, methylnaphthalene, biphenyl, and dimethylnaphthalene. Other oxygen-containing products included benzaldehyde, benzofuran, methylbenzofuran, dibenzofuran, diphenyl ether (or phenylphenol), cresol, ethylphenol, and 2-hydroxyphenyl-2-phenylpropane (8).

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MONS 020501

Section 6

MATERIALS CONTAINING ONLY C AND H OR C, H, AND O

BISPHENOL A EPOXY RESIN

CASRN. 25068-38-6

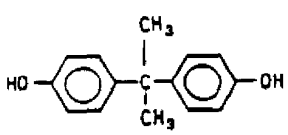
Synonyms: Bis(p-hydroxyphenyl)dimethylmethane-epichlorohydrin copolymer; 2,2-Bis(p-hydroxyphenyl)propane-epichlorohydrin condensate; Diphenylolpropane-epichlorohydrin polymer; Epichlorohydrin-bisphenol A epoxy resin; Oxirane, (chloromethyl)-, polymer with 4,4'-(1-methylethylidene)bis[phenol]; Phenol, 4,4'-(1-methylethylidene)bis-, polymer with (chloromethyl)oxirane, Propane, 1-chloro-2,3-epoxy-, polymer with 4,4'-isopropylidenediphenol.

Trade Names: Araldite 6005 (or 6010 or 6084 or GY250 or GY260 or GY280); Bakelite PKOA; Casting Resin F; Epikote 828 (or 834 or 836 or 1004 or 1007), Epi-Rez 510; Epon 826 (or 834 or 1001 or 1002 or 1004); Epotuf 37-139; GenEpoxy 190

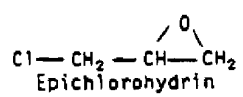
General Information

Molecular Formula: $(C_{15}H_{16}O_2 \cdot C_3H_5ClO)_x$

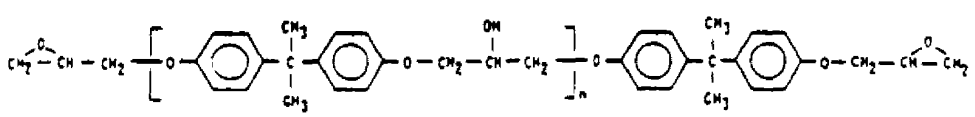
Structure of Monomers and Polymer:



Bisphenol A



Epichlorohydrin



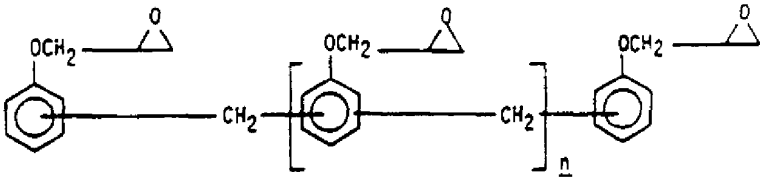
Most commonly, the polymer shown is cured with a cycloaliphatic anhydride or amine as a hardener to effect crosslinking. "The largest producer of resins for use in

casting transformer coils used in the United States reports that roughly 80% of their production for transformer coils may be approximated by the above generalities. The remainder usa cycloaliphatic compounds in place of bisphenol A (1) "

Uses Epoxy resins are a type of solid dielectric that may "be cast or impregnated into the coils of a transformer, used as films in capacitors, or used as insulation for various parts of transformers, capacitors, or other electrical equipment" (1) Epoxy insulation systems have been used in transformers since the early 1960s (2)

Thermal Decomposition Mechanisms

Bisphenol A epoxies are less stable than epoxy novolak resins, which are produced from phenol-formaldehyde resins and epichlorohydrin, because the isopropylidene linkages in the former are less stable than the methylane linkages of the epoxy novolaks. The structure of a novolak epoxy is as follows (3).



Isomerization of terminal epoxide groups before cleavage would give 2-hydroxypropanal [$CH_3CH(OH)CHO$] and propionaldehyde (CH_3CH_2CHO). Direct cleavage in the end groups would give ethylene oxide and formaldehyde. Acetaldehyde (CH_3CHO) could arise from isomerization of ethylene oxide. Chlorosubstituted compounds probably arise from impurities in the glycidyl portion of the resin (4)

Summary of Experimental Studies Reviewed

Because of the scarcity of information on thermal degradation of bisphenol A epoxy resins, information is also included on the structurally similar epoxy novolak resins.

Pyrolysis Pyrolysis of a novolak epoxy resin at 350°C gave toluene (the reaction solvent) and water as major volatiles (94%). Phenol, cresols, and higher phenols ethane, allyl chloride, aldehydes, and ketones were among the pyrolysis products (4) Pyrolysis of a bisphenol A epoxy resin cured with 2 6 parts per hundred resin

2-ethylimidazole at 380 to 425°C gave mostly phenol, diphenyl ether ($C_6H_5OC_6H_5$), and C_1- to C_5-alkylated phenols and aromatic ethers. Most diphenylpropane derivatives were p,p'-isomers (5).

Pyrolysis of uncured bisphenol A epoxy at 350 to 450°C gave water (from condensation of epoxide groups) and toluene (reaction solvent) as the major products. At 450°C, approximately equal amounts of methyl chloride (CH_3Cl) and acetaldehyde were formed. High-boiling cresols, phenol, isopropenylphenol [$CH_3C(CH_2)C_6H_4OH$], and bisphenol A were in the residue (4).

Major products from pyrolysis of a bisphenol A epoxy resin cured with methylenedianiline ($H_2NC_6H_4CH_2C_6H_4NH_2$) were water at 350°C and water, CO, CH_3CHO, CH_3Cl, and CH_4 at 450°C. Methylcyclopentadiene arose from both cured and uncured bisphenol A epoxies (4).

Pyrolysis of an uncrosslinked novolak epoxy resin at 360 to 1200°C volatilized 38 to 57% of the resin; 51 to 82% of the volatiles comprised an uncharacterized material (average molecular weight 350 from pyrolysis at 800°C). Methyl chloride (CH_3Cl) and ethyl chloride (C_2H_5Cl) were found in the volatile fraction at 360°C, but not at higher temperatures. Hydrogen (H_2), ethylene (C_2H_4), and substituted-cyclopentadienes were detected in the volatile fraction at 800 and/or 1200°C, but not at 360 or 500°C. In contrast to what would be expected from combustion, CO concentrations in the volatile fraction increased with increasing temperatures (maximum 25.9% at 1200°C) as CO_2 concentrations decreased (maximum 16.2% in the volatiles at 360°C). Organics representing more than 3% of the volatiles were methane (CH_4, 4.3% at 1200°C), propylene ($H_2C{=}CHCH_3$, 6.5% at 360°C), benzene (C_6H_6, 8.1% at 1200°C), and methyl chloride (CH_3Cl; 5.1% at 360°C). Other organics present at less than 3% of the volatile fraction at one or more pyrolysis temperatures were acetylene (C_2H_2), acetone (CH_3COCH_3), propane (C_3H_8), and ethane (C_2H_6) (Madorsky and Straus, 1961; cited by Zbozinek, 1985) (1).

An epoxy resin used to impregnate tapes and wrapper insulation in dry-type transformers was pyrolyzed at 600 and 1000°C. The products collected (in unreported amounts) were CO_2, CH_4, C_2H_4, propylene, butylene (1-butene?), pentane, cyclopentadiene, toluene, phenol, xylene, styrene, indan, indene, naphthalene, and biphenyl (6).

Lum and Feinstein (1981, 1982, cited by Zbozinek, 1985) (1) found benzene, phenol, and cresol in the thermal degradation products of novolak epoxies (pyrolysis?) heated at 300 to 500°C.

Combustion Bisphenol A epoxy resins are more combustible than comparable thermosetting plastics, having a lower tendency to carbonize The resins continue to burn on their own when removed from the ignition source. The odors of phenol, formaldehyde, and hardeners are detected in the smoke (4).

Approximately 500 lb (230 kg) bisphenol A epoxy is used in the cast transformer coils of a 3-phase transformer. The example is based on a 2,000 kVA model with three high-voltage and three low-voltage coils rated at 12,000 VAC and 480 VAC, respectively The transformer cabinet with a volume of 347 ft^3 (9 83 m^3), 208 ft^3 (5 89 m^3) of which is occupied by air, if unventilated (but most utility transformer cabinets are), contained sufficient oxygen to combust only 1.5 lb (0.7 kg) of the resin. When heated for 30 min at temperatures up to 500°C with sufficient oxygen for complete combustion, resin samples produced 20 identified and 30 unidentified compounds. The latter were in "extremely low" concentrations The major products were 26.0 ppm (based on resin weight) phenol (C_6H_5OH), 2 6 ppm toluene ($C_6H_5CH_3$), 2.0 ppm ethylbenzene ($C_6H_5C_2H_5$), and 1.5 ppm benzene (C_6H_6) The rest of the mass was not accounted for by the study authors. Estimated concentrations in air were 3 03 mg phenol/m^3 (OSHA permissible exposure limit [PEL] = 19 mg/m^3), 0.30 mg toluene/m^3 (PEL = 375 mg/m^3), and 0 23 mg ethylbenzene/m^3 (PEL = 435 mg/m^3) (2).

Acetylene (C_2H_2), benzene, toluene, and an aromatic fraction were detected in the gases from combustion of an 800 kVA GEAFOL cast resin transformer at 1000 to 1200°C The fires were initially fueled by propane and wood, and the gases from the fuels were not separated from the gases evolved from combustion of the transformer (Altmann et al., 1984; cited by Zbozinek et al , 1985) (1).

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CROSSLINKED POLYETHYLENE

CASRN. 68584-45-2 [for radiation crosslinked homopolymer; none available for peroxide-crosslinked homopolymer].

Synonyms: XLPE; Ethene, homopolymer, radiation crosslinked.

Trade Names (producers). None found

General Information

Molecular formula: $(C_2H_4)_n$

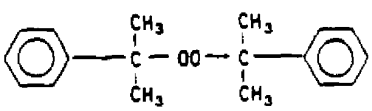
Structure of Monomer, Polymer, and Common Peroxide Crosslinking Agent

$CH_2.CH_2$

Ethylene

$\sim CH_2CH_2CHCH_2CH_2\sim$
$\sim CH_2CH_2CHCH_2CH_2\sim$

Radiation-Crosslinked Polyethylene (XLPE)



Dicumyl Peroxide (DCP)

In cable manufacture, crosslinking is done immediately after extrusion of the cable insulation because the material cannot be shaped after crosslinking This crosslinking is done almost exclusively by adding peroxides such as dicumyl peroxide (DCP) to low-density polyethylene granulate and steam curing for about 1 min at

about 170°C. Electron beam or gamma irradiation are other methods of crosslinking polyethylene (1,2). Radiation curing of high-density polyethylene is limited to low-voltage cables with thin insulation. Because moisture degrades the service life of XLPE, steam curing may be replaced by treatment with pressurized, heated inert gas (3).

Uses. Low-density grades are used for wire and cable coatings and insulation, high-density grades for pipe and molded fittings. Since the 1970s, most of the distribution power cables installed in the range 15 to 46 kV have been insulated by chemically crosslinked polyethylene. These XLPE cables are substitutes for oil-impregnated paper-insulated lead-covered cable. By mid-1971, the use of polyethylene for power cables was 400 million pounds (9×10^8 g), the rapid growth in this use surpassing the use of crosslinked polyethylene for communications cables at that time. Use in coaxial and other cables was much less than 100 million pounds (2.2×10^8 g). Power utilities have widely accepted XLPE-insulated cable for transmission circuits at operating voltages up to at least 138 kV (2). XL-E or thermoset polyethylene may be used as an integral covering for low-voltage applications on very small diameter single-conductor cables (3). Crosslinked polyethylene may also be used in heat-shrinkable tubing to insulate joints and splices of hook-up wire (4).

Thermal Decomposition Mechanism:

No specific information was found for crosslinked polyethylene; but since crosslinking is involved in thermal degradation of linear and branched polyethylenes, the thermal decomposition mechanisms of XPLE are probably similar to those for polyethylene (see page 6-12).

Summary of Experimental Studies Reviewed

Pyrolysis. Unfilled crosslinked polyethylene insulation from a No. 14 small wire lost 3.4% of its initial weight when heated from room temperature to 393°C at the rate of 10°C/min, 48.9%, when heated to 453°C, and 97.5%, when heated to 467°C. Another DCP-crosslinked polyethylene sample lost 2.0% of its weight by 361°C and 98.7% by 481°C. A sample with 33% filler showed about the same weight loss with increasing temperatures (5).

DC- decomposition products and additives present in the crosslinked polyethylene are likely to be identified among pyrolyzates at low temperatures. Crosslinked polyethylene from three cables that had failed after 9 or 11 years of service

found to contain several compounds at the parts per million level. Acetophenone, an expected degradation product of DCP, was not found in any of the three samples. In one sample, α-methylstyrene was the major contaminant and cumene was the second most important contaminant. In the two other samples, thiobutyric acid S-decyl ester was the major contaminant followed by phenol and cumyl alcohol (or vice versa). Other impurities found in one or two of the three samples included cumene, toluene, dipropropylene glycol methyl ether, acetophenone, phthalates, chloroform, and benzene. Uncrosslinked polyethylene from a fourth cable contained thiobutyric acid S-decyl ester, phenol, and toluene (all identifications were made by gas chromatography-mass spectrometry) (6).

Combustion. No specific information was found on XLPE combustion or other thermal oxidation.

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KRAFT PAPER

General Information

Molecular Formula $(C_6H_{10}O_5)_n$

Structure of Polymer: 88 to 91% alpha-cellulose, 1 to 3% hemicellulose, and 2 to 5% lignin.

MONS 020508

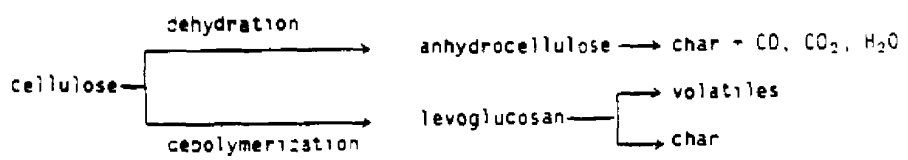
Uses· Electrical use for kraft paper is for insulation in oil-immersed equipment such as transformers. To upgrade the thermal resistance, the kraft paper may be modified by cyanoethylation, amine treatment, etc Additives such as morpholine, oxyalkylamine, aromatic polyamines, p-toluene sulfone (?), and carbamates have been used or suggested (1).

Oil-impregnated paper is used to insulate overhead distribution cables (2) and is the standard insulation for 115-550 kV circuits, whereas extruded solid-dielectric insulation prevails over paper insulation for intermediate voltage cables (15 to 69 kV) Use of paper insulation in the intermediate range will probably continue because of the need to maintain existing installations and its desirable characteristics such as long service life (3).

Thermal Decomposition Mechanisms

Cellulose pyrolyzed at rapid heating rates primarily degrades by chain cleavage Segments decompose to give a syrup whose major component is levoglucosan (1,6-anhydro-β-D-glucopyranose) and its furanose isomer (1,6-anhydro-β-D-glucofuranose) Numerous lower molecular weight products form at temperatures ≥ 500°C Ash in trace amounts appears to catalyze condensation, dehydration, and fragmentation reactions, thereby reducing syrup yields. Primary syrup products can be converted to ethylene and other important industrial chemicals

Nonspecific thermal decomposition reactions occur Anhydrosugar derivatives are formed by intramolecular transglycosylation reactions, which compete with dehydration, fragmentation, and condensation reactions. These competing reactions lead to low molecular weight gases, char, and numerous other products Low heating rates and long residence times reduce the yields of more desirable sugar derivatives (4)



Summary of Experimental Studies Reviewed

Pyrolysis Product gases from pyrolysis of kraft paper are produced in about the same amounts as from pyrolysis of other cellulose sources, including woods The

gases are CO_2, CO, H_2, C_2H_2 (acetylene), CH_4 (methane), C_2H_4 (ethylene), and other hydrocarbons (5) Depolymerization gives the anhydroglucose product levoglucosan (a glucopyranose derivative) and its furanose analog. Temperetures above 500°C give numerous lower molecular weight products and char. Dehydration reactions give anhydrocellulose, which also decomposes to give char and volatiles (4).

Combustion No information was found on specific products of kraft paper combustion

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POLYETHYLENE

CASRN 9002-88-4

Synonyms: Polythene, ethylene homopolymer; ethene homopolymer

Trade Names: Agilene; Alathon; Alkathene; Courlene, Lupolen; Platilon, Pylen, Reevon (1)

General Information

Molecular Formula: $(C_2H_4)_n$

MONS 020510

HLTH: Methemoglobinemia (13)
Acute systemic effects (4)
Suspect carcinogen
IARC CARC: Animal and Human Indefinite, '78
Human Suspect, '82
SKIN IRR Moderate
INGES ACUTE. Mouse LD_{50}. 520 mg/kg

p-Toluidine (CRE)
CASRN: 106-49-0
DESC: Solid, m.p. 45-47°C
SKIN IRR: Rabbit: 500 mg/24 H, severe
EYE IRR: Rabbit: 20 mg/24 H, severe
MUTAGEN
ORAL: Rat LD_{50}: 56 mg/kg

3-Tolunitrile; m-Tolunitrile; 1,3-Tolunitrile (NOM)
CASRN: 620-22-4
DESC: Semivolatile Liquid
EYE IRR: Rabbit: 500 mg/24 H, severe
ORAL: Rat LD_{50}: 4.2 g/kg

Trifluoroacetyl fluoride (TEF)
CASRN: 354-34-7

Trifluoromethane (NIT)
CASRN: 75-46-7

Trimethylbenzene (SUL)
CASRN: 25551-13-8
STDS: TLV: 25 ppm, 125 mg/m³ TWA, 35 ppm, 170 mg/m³ STEL
DESC: Semivolatile Liquid
HLTH: Irritation-Lungs, Skin--Marked (14).
Cumulative CNS Effects (7). Anemia (12)
SKIN IRR: Yes

Triphenylene (PE)
CASRN: 217-59-4
DESC: Solid, m.p. 195-198°C

Valeraldehyde; Pentanal; Amyl aldehyde (PE)
CASRN: 110-62-3
DESC: Volatile Liquid
SKIN IRR: Rabbit: 500 mg/24 H, moderate
EYE IRR: Rabbit: 500 mg/24 H, severe
ORAL: Rat LD_{50}: 3200 mg/kg
SKIN: Rabbit LD_{50}. 6000 mg/kg

Valerolactone (PE)
CASRN: (γ-isomer) 108-29-2; (δ-) 542-28-9
DESC: Semivolatile Liquid

Vinyl benzoate (PET)
CASRN: 769-78-8
DESC: Semivolatile Liquid
ORAL: Rat LD_{50}: 3250 mg/kg
SKIN IRR: Rabbit: 10 mg/24 H

Vinylcyclohexene (NIT)
CASRN: 695-12-5
DESC: Volatile to Semivolatile Liquid
ORAL: Rat LD_{50}: 3080 mg/kg
IARC CARC: Animal Indefinite, '76.

Vinylidene fluoride; 1,1-Difluoroethene (TFZ, VIT)
CASRN: 75-38-7
DESC: Gas
ORAL TUMORIGEN: Rat TD_{L_o}: 1930 mg/kg/52 W
INHL: Rat LC_{L_o}: 128,000 ppm/4 H

Vinylpyridine (PU)
CASRN: (2-isomer) 100-69-6; (4-) 100-43-6
DESC: Semivolatile Liquid

Vinyltoluene; Methylstyrene (NOM, PET)
CASRN: 25013-15-4
STDS: OSHA: 100 ppm, 480 mg/m³
TLV: 50 ppm, 240 mg/m³ TWA; 100 ppm, 485 mg/m³ STEL
DESC: Semivolatile Liquid
HLTH: Irritation-Eyes, Nose, Throat, Skin--Moderate (15, Less than 200 ppm)
CNS effects (7, Greater than 200 ppm).
INGES ACUTE: Rat LD_{50}: 4000 mg/kg

Xylenes (CSPE, EPO, NOM, PU)
CASRN: 1330-20-7
STDS: OSHA: 100 ppm, 435 mg/m³
TLV: 100 ppm, 435 mg/m³ TWA; 150 ppm, 555 mg/m³ STEL
DESC: Semivolatile Liquid
HLTH: Irritation-Eyes, Nose, Throat, Skin--Moderate (15, Less than 200 ppm)
Narcosis (8, Greater than 200 ppm).

Xylenols (CRE)
2,3-
CASRN: 526-75-0
DESC: Solid, m.p. 73-75.5°C
2,4-
CASRN: 105-67-9
DESC: Solid, m.p. 22-23°C/Semivolatile Liquid
2,5-

CASRN: 95-87-4
DESC: Solid, m.p. 71-73°C

2,6-
CASRN: 576-26-1
DESC: Solid, m.p. 45-46°C

3,4-
CASRN: 95-65-8
DESC: Solid, m.p. 65-68°C

3,5-
CASRN: 108-68-9
DESC: Solid, m.p. 65-66°C

Xylidine; Dimethylaniline (CRE)
CASRN: 1300-73-8
STDS: OSHA: 5 ppm, 25 mg/m^3
TLV: 2 ppm, 10 mg/m^3 TWA
DESC: Semivolatile Liquid
HLTH: Methemoglobinemia (13)
Acute systemic toxicity (4)
SKIN ABS: Yes
INGES ACUTE: Rate LD_{50}: 610 mg/kg

2,4-Xylidine (CRE)
CASRN: 95-68-1
DESC: Semivolatile Liquid
MUTAGEN
IARC CARC: Animal Indefinite, 178

2,5-Xylidine (CRE)
CASRN: 95-78-3
DESC: Semivolatile Liquid
MUTAGEN
ORAL: Rat LD_{50}: 1297 mg/kg
IARC CARC: Animal Indefinite, '78

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MONS 020590

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Structure of Monomer and Polymer

$CH_2.CH_2$ $\quad\quad$ $-(CH_2CH_2)_{\overline{n}}$

Ethylene (ethene)

Linear, high-density polyethylene is produced by polymerization in the presence of transition metal catalysts (e g , chromium oxide or molybdenum oxide on a silica-alumina support) at relatively low temperatures and pressures. Incorporating butene, hexene, or another α-olefin as a comonomer lowers the density of the product Low-density polyethylene, with a relatively high degree of branching, is produced by use of higher pressures and temperatures and peroxide-type catalysts Incorporating polar comonomers such as vinyl acetate modifies the properties of the product. Linear low-density polyethylene is produced by copolymerization of ethylene with α-olefins such as butene, hexene, or octene at high or low pressures High-molecular-weight low-density polyethylene and high-molecular-weight high-density polyethylene are two other types. The latter is a linear homopolymer or copolymer with weight average molecular weight 200,000 to 500,000 They have a density greater than 0.941 g/cm^3 (2).

The density of low-density polyethylene falls in the range 0 910-0 925 g/cm^3, that of medium-density polyethylene, 0.926-0.940 g/cm^3 Copolymer high-density polyethylene has a density 0.941-0.959 g/cm^3. Homopolymer high-density polyethylene has a density of at least 0.960 g/cm^3 (2).

Polyethylenes are also categorized according to the manufacturing method, i e , whether high, medium, or low pressure was used High-pressure polyethylene includes low-density polyethylene and medium-density polyethylene up to a density of ~ 0.933 g/cm^3 Low-pressure polyethylene includes medium-density polyethylene from a density of ~ 0 933 g/cm^3 through high-density polyethylenes with densities up to > 0 96 g/cm^3. Medium-pressure polyethylene have high densities (~ 0 95-~ 0 96, (2)

Uses Polyethylene uses include coatings, containers, toys, liners, bags, and pipe and tubing as well as the electrical applications Resins with melt indexes of 0 2 to 0 ~ g 10 min are used as wire and cable coatings in thicknesses ranging from 0 005 to 0 5 in (0 13 to 13 mm) Polyethylene insulation and jacketing is used on high voltage power cable telephone cable, television lead-in cable and coax cable A linear low-dens ty polyethylene which is a copolymer of ethylene with

various α-olefins, may also be used for wire and cable insulation and jacketing High-molecular-weight high-density polyethylene, which may be either homopolymers (highest density) or copolymers (typical monomers are butene, hexene, and octene), is used for cable conduit and other pipe (2)

Polyethylene, crosslinked polyethylene, ethylene-propylene rubber, and butyl rubber are used for extruded cable insulation. Polyethylene has a low power dissipation factor, high volume resistivity, high breakdown strength, and ozone and weathering resistance, but it is susceptible to environmental conditions above 75°C A major use for polyethylene in the electric power industry in the United States is for duct or pipe for installing buried cable. The duct material, called combined duct cable or CD cable, is usually black, low- or medium-density polyethylene (3) Crosslinked polyethylene (XLPE) is widely preferred for extruded cable insulation and accounts for most of the increase in the use of polyethylene in distribution power cables since 1967 (4) Crosslinked polyethylene is discussed on page 6-5

Polyethylene used in buried underground distribution cables (15,000 to 25,000 V) has experienced a high rate of intolerable failures after service for 5 to 7 years The low cost still makes use of polyethylene attractive. Research continues to find additives to improve the service life. Polyethylene has been used for years as low-loss insulation in high-frequency, coaxial cables for electronic applications Polyethylene is also used in ocean telephone and telegraph cables and direct-buried cathodic-protection circuits and telephone cables (5) However, polyethylene is impractical for use in high-voltage, power transmission cables

Cable jackets made of polyethylene are used when moisture resistance is the primary requirement, such as for nonleaded dry paper or plastic-insulated telephone cables. Use of polyethylene jackets for lead-sheathed underground power cables facilitates pulling the cable into ducts High-molecular-weight polyethylene (molecular weight about 30,000 amu) is used to avoid stress cracking If the covering is to be exposed to weather, a filling of about 2% carbon black must be added to prevent ultraviolet-radiation cracking (5)

Polyethylene can also be used for insulating moldings (5)

MONS 020512

Thermal Decomposition Mechanisms

Pyrolysis. In the absence of oxygen, polyethylene undergoes crosslinking at about 200 to 290°C and decomposes at temperatures above 290°C Scission reactions compete with crosslinking reactions and are favored at higher temperatures Thermal decomposition of polyethylene creates fragments with molecular weights up to about 700 Thermal cracking of polyethylene gives good yields of high-melting waxes (molecular weights greater than 400) without char or tar formation (7)

Polyethylene degradation is accompanied by a rapid decrease in the polymer's molecular weight. Little monomer is produced by depropagation reactions (i e , the reverse of the free radical addition reaction that produced the polymer) Monoolefins are produced by intramolecular transfer of hydrogen atoms to a carbon radical, the six-membered ring transition state favors the formation of 1-hexene Larger fragments form in intermolecular transfers Peroxide links present in the polymer from slight oxidation during preparation, storage, and processing facilitate the free radical formation. Other weak links in the polyethylene structure are carbonyl groups, chain branches, and unsaturated structures (8)

Combustion. Thermal oxidation of polyolefins and other hydrocarbons (RH) involves generation of a hydrocarbon radical ($R^{\cdot}$); reaction of the hydrocarbon radical R with oxygen ($^{\cdot}OO^{\cdot}$) to give a peroxy radical $ROO^{\cdot}$, propagation of the reaction by abstracting $H^{\cdot}$ from another or the same hydrocarbon molecule, thereby producing a new hydrocarbon radical $R'^{\cdot}$; and reaction of $R'^{\cdot}$ with $^{\cdot}OO^{\cdot}$ to give a new peroxy radical $R'OO^{\cdot}$ Peroxy radicals can also abstract $H^{\cdot}$ from RH, giving ROOH ROOH decomposition gives $RO^{\cdot}$ and $HO^{\cdot}$, which can also participate in the chain reaction with RH (7)

Summary of Experimental Studies Reviewed

Pyrolysis Pyrolysis of polyethylene at temperatures up to 1000°C gives saturated (paraffins, alkanes) and unsaturated hydrocarbons (olefins, alkenes, and dienes) The olefins are primarily 1-alkenes (α-olefins) with lesser amounts of α,ω-dienes Products having up to 18 carbons have been identified, some studies have reported products whose chain lengths extended to 30 or more carbons (9 10)

Generally, major paraffin and α-olefin pyrolysis products throughout the temperature range studied had no more than seven carbons. Hydrogen was reported to be a major volatile product at 1000°C (11). α,ω-Olefins (α,ω-dienes), olefins with non-terminal double bonds, and aromatics were generally trace to minor products. Products with more than 21 carbons were predominantly straight-chain hydrocarbons for low-density polyethylene and olefins for high-density polyethylene (10).

The experimental pyrolysis studies we reviewed are summarized in Table 6-1.

Combustion. Polyethylene may undergo slight thermooxidative degradation at processing temperatures up to 320°C. Heating polyethylene below about 300°C caused a slight weight loss (up to about 4%). Volatile products largely accounting for the loss were water, ethylene, and low-molecular-weight alcohols, aldehydes, ketones, and carboxylic acids (20, citing older work). Oxygen-containing compounds were major products up through at least 350°C but were minor products between 350 and 700°C, indicating that pyrolytic processes dominated in this region. At 1000°C, two ketones--hexanone and octanone--were among the major volatile products (21).

Olefins and paraffins were intermediate-to-major products throughout the temperature range reviewed (≤ 1000°C). At the higher temperatures, the α-olefins were generally long-chain hydrocarbons, whereas the dienes and paraffins had shorter chains (18).

Only one reference (22) reported that carbon dioxide (50 to 74% yield) and carbon monoxide (20 to 21%) were major combustion products, with 19% ethylene, about 7% methane, and 1 to 3% acetylene comprising the remaining volatiles produced at 700°C.

Soot was also an intermediate-to-major combustion product, having yields of 6 to 25% (based on the weight of the dried soot and the weight of the unburned sample) at 600 to 900°C. The yields of aromatic products increased with increasing temperature. They were found mainly in soot and cold-trapped liquids. Benzene derivatives without condensed rings, such as styrene and ethylbenzene, were products formed in intermediate yields at 1000°C. Their yields were usually minor at lower

Table 6-1

POLYETHYLENE PYROLYSIS

Product	Formula	372-392°C 4 5 0 5 hr in vacuo [12]	400°C [13,14][b]	420°C, [9,15][b]	510°C [36]	600°C [7]	600°C [17]	1000°C [18]	1000°C [31][b]	Laser Pulse [39]
Weight loss		49-83%[a]								
Liquid residue	> C_{40}	✓								
Carbon dioxide	CO_2								Minor	
Hydrogen	H_2								53 3%	
Paraffins			35 40%	64% of C_{10-30}						
n Hydrocarbons								✓		
C_1 C_2 alkanes and/or alkenes				Major						
C_3 C_4 alkanes and/or alkenes					Major					
C_5 C_6 alkanes and/or alkenes										Major
C_{12} alkanes and/or alkenes								✓		
C_{13} alkanes and/or alkenes						✓				
C_{14} alkanes and/or alkenes										✓
C_{15} alkanes and/or alkenes							✓			
C_{16} alkanes and/or alkenes		✓								
Cyclic alkanes		✓				Trace				
Dimethylalkanes						Trace				
Dimethylalkenes						Trace				
Methane	CH_4								41 2%	
Ethane	C_2H_6								Minor	
Olefins			59%						Minor	
α olefins (1 alkenes)	RCH CH			3% of C_{10-30}				Major		
Ethylene	C_2H_4								Minor	
Propene	C_3H_6						✓		Trace	
1 Pentene	C_5H_{10}				Major		Major			
1 Hexene	C_6H_{12}		30 41%		Major		Major			
1 Heptene	C_7H_{14}				Major					
Alkenes with nonterminal double bonds	RCH CHR'			5% of C_{10-30}		✓				
α ω Dienes (Olefins)	H_2C $CH(CH_2)_nCH$ CH_2			Trace[c]				✓		
Acetylene	C_2H_2								Minor	
Aromatics			< 5%							
Benzene	C_6H_6		✓			Trace			0 9%	
Toluene	$CH_3C_6H_5$		✓			Trace			Trace	
Ethylbenzene	$C_2H_5C_6H_5$		✓				✓			
Styrene	CH_2 CH C_6H_5						✓			
Xylenes	$C_6H_4(CH_3)_2$						✓			
Naphthalene	$C_{10}H_8$						✓			

[a] Based on original polymer weight

[b] Based on volatiles recovered

[c] Percent not quantitated here

temperetures. The yields of individual polycyclic aromatic hydrocarbons (PAHs, condensed benzene derivetives) rose from ebout 0 01% et 600°C to about 0 1% at 900°C Yields were based on the original polymer sample weight. At 900°C, the concentration of benzo[e]pyrene (B[a]P) was 1 06% in the dried soot compered to ≤ 0 041% in urban air particulates It should be noted that elthough the amount of B[e]P produced per gram of polyethylene was about the seme as that produced per gram of polystyrene, the B[e]P concentretion in polyethylene soot was three to four times greater beceuse polystyrene produced three to four times as much soot as did polyethylene (23)

About 50% of the PAHs in the smoke particulates from either flaming or nonflaming (smoldering) combustion of polyethylene was pyrene. The only other major PAH that was formed during nonflaming combustion was $C_{14}H_{10}$ (anthracene or phenanthrene) Flaming combustion gave a wider variety of PAHs (24). At 950°C, the concentrations of individual PAHs and other aromatics caught in cold traps were < 1 to about 4% (based on the weight of the total condensate, whose amount relative to the initial polymer weight was not given) except for naphthalene at 13 5% (14) The PAHs identified that are carcinogens included benz[a]anthracene, benzo[b]fluoranthene (2,3-benzofluoranthene), benzo[c]phenanthrene, benzo[a]pyrene, benzo[e]pyrene, and chrysene.

Studies reviewed on the thermooxidation and combustion of polyethylene are summarized in Tables 6-2 and 6-3

Table 6-2

POLYETHYLENE COMBUSTION OR OTHER THERMOOXIDATIVE DEGRADATION AT TEMPERATURES UP TO 700°C

Product	Formula	200°C (20)	260 deg°C (20)	300°C (13,19)	350°C (25)	Temperature Dependence of Product Yield: 400°C (25)	450 500°C (26)	500 600°C (25)	600°C (27)	650°C (23)	650°C (21,25)	650°C (24)	700°C (23)	700°C (22)
Weight loss			~ 0%				5 - 10%							
Oxybenzoic														
Total volatiles recovered														
Gases														
Coal											6.25%		~ 4.5%	
Carbon monoxide	CO									f				20.21%
Carbon dioxide	CO_2									f				40.34%
Water	H_2O	f	f											
Low molecular weight alcohols	ROH	f	f											
Ethanol	C_2H_5OH	f		f										
Acids, others			f											
Ketone	C_3H_6O		f											
Tetrahydrofuran	C_4H_8O		f											
Epoxy compounds (tentative)				f										
Formaldehyde	HCHO		Major 900 2300		Max between 250 & 600°C									
Aldehydes	RCHO		f							Minor		f		
Acetaldehyde	CH_3CHO	f	Major 1370 2400						Major (ethene) 1 600 ppm					
Propionaldehyde	CH_3CH_2CHO	f	270 440											
Acrolein	CH_2 CHCHO		230 170	f				Max at ~ 55 O_2		f				
1-Butyraldehyde	C_4H_8O		f											
n-Butyraldehyde	$CH_3CH_2CH_2CHO$	f	700											
Furfural	$CH_2(CH)_2COCHO$		540											
Benzal	$C_6H_5(CH)_2CHO$								f					
C_3-C_6 saturated and unsaturated aldehydes									f					
C_3-C_{10} aldehydes				< 2%										
C_3-C_{12} aldehydes				< 40%										
Ketones	RCOR'		f	< 2%						Minor		f		
Acetone	CH_3COCH_3		250						f					
Methyl ethyl ketone	$CH_3COCH_2CH_3$		120											
Methyl vinyl ketone	CH_3COCH CH_2		50											
Methyl propyl ketone	$CH_3COCH_2CH_2CH_3$	f	290	f										
Benzenone	C_6H_5O			f										
Butenone/Fe Oxides	C_4H_6O			f					f					
Carboxylic acids	RCO$_2$H		f											
Formic acid	HCO_2H	f	Major 2400 4170											
Acetic acid	CH_3CH_2H	f	Major 870 1760			Max between 300 & 600°C								
Propionic acid	$CH_3CH_2CO_2H$		660 300											
Butyric acid	$CH_3CH_2CH_2CH_2H$		85 300											
Acrylic acid	CH_2 $CHCH_2H$		170 100	< 1%										

[illegible]

Table 6-2 (continued)

Product	Formula	Temperature Dependence of Product Yield												
		< 200°C (29)	200-300°C (30)	300°C (11,14)	350°C (25)	400°C (25)	450 500°C (26)	450 600°C (25)	500°C (27)	600°C (21)	600°C (23,25)	650°C (24)	700°C (21)	700°C (22)
Isovaleric acid	$(CH_3)_2CHCH_2CO_2H$		✓											
Isobutyric acid	$CH_3CH(CH_3)CO_2H$		✓											
Caproic acid	$CH_3(CH_2)_4CO_2H$		✓											
Hydroxy carboxylic acid esters			✓											
Hydroxybenzoic acid	$C_6H_4(OH)CO_2H$		✓											
Terpenes (cyclic esters)	-		✓											
Butylcyclohexane	$C_{10}H_{20}$		200											
Polycyclanes	$C_{10}H_{18}$		✓											
Paraffins (alkanes) (straight/saturated hydrocarbons)	C_nH_{2n+2}			< 6 [3]%							< 69 [26]			
Short chain paraffins	C_nH_{2n+2}									✓				
Methane	CH_4													6.5 [7]%
Ethane	C_2H_6													
Cyclic alkanes	C_nH_{2n}									✓		✓		
Cyclic alkanes	C_nH_{2n-2}											✓		
Cycloparaffins	C_nH_{2n}		✓											
Paraffins (hydrocarbons unsaturated by one or more double bonds)				< 32 [25]%								✓		
n-Olefins (alkenes)	C_nH_{2n}		✓	✓					✓	✓		✓		✓
Ethylene	C_2H_4	Major								✓				< 4%
1-Pentene	C_5H_{10}		✓	✓					✓			✓		
1-Hexene	C_6H_{12}		✓	✓					✓			10 [8]%		< 1 [3]
Acetylene	C_2H_2													
n-Olefins (alkenes)	C_nH_{2n-2}									✓		✓		
Cyclic alkenes	C_nH_{2n-2}													
Long chain olefins														
Short chain alkenes	C_nH_{2n}									✓				
Two unidentified isomers	$C_{10}H_{16}$													
C_6-C_{10} hydrocarbon liquid							✓							
Benzene	C_6H_6			< 0.5%						✓		5 [8]%		
Toluene	$CH_3C_6H_5$			< 1%						✓		3 [8]		
Ethylbenzene	$C_6H_5C_2H_5$			< 0.5%						✓		2 [5]		
Xylenes	$C_6H_4(CH_3)_2$									✓				
Styrene	$C_6H_5CH=CH_2$									✓				
Ethylbenzene	$C_6H_5C_2H_5$									✓				
Biphenyl	$C_6H_5C_6H_5$													
Indene	C_9H_8													
Indane	C_9H_{10}													
Naphthalene	$C_{10}H_8$													
1-Methylnaphthalene	$CH_3C_{10}H_7$													
2-Methylnaphthalene	$CH_3C_{10}H_7$													
1-Phenylnaphthalene	$C_6H_5C_{10}H_7$													

[illegible]

Table 6-2 (continued)

Temperature Dependency of Product Yield

Product	Formula	[illegible] (20)	364-384°C (20)	[illegible] (13,24)	[illegible] (25)	400°C (25)	400-500°C (26)	500-600°F (25)	600°C (27)	664°C (23)	664°C (23,25)	700°C (24)[a]	760°C (21)	780°C (22)[b]
Benzo[a]thiophene	C_8H_6S													
Fluorene	$C_{13}H_{10}$													
9-Methylfluorene	$CH_3C_{13}H_9$													
Phenanthrene	$C_{14}H_{10}$													
4,5-Methylenephenanthrene	$C_{15}H_{10}$													
Methyl-9,5-methylenephenanthrene	$C_{16}H_{12}$													
Methylphenanthrene	$CH_3C_{14}H_9$													
Anthracene	$C_{14}H_{10}$													
Dihydroanthracene	$C_{14}H_{12}$										< 0.01%			
Tetrahydroanthracene	$C_{14}H_{14}$										< 0.01%			
Pyrene	$C_{16}H_{10}$										< 0.01%			
Methylpyrene	$C_{17}H_{12}$													
Benzanthracene (see text phenylnaphthalene)	$C_{18}H_{12}$													
Benzo[c]phenanthrene	$C_{18}H_{12}$													
7,8-Benzofluorene	$C_{17}H_{12}$													
1,2-Benzofluorene	$C_{17}H_{12}$										< 0.01%			
Chrysene	$C_{18}H_{12}$													
7,8-Benzofluoranthene	$C_{20}H_{12}$													
Benzo[a]pyrene	$C_{20}H_{12}$										< 0.01%		< 0.01%	
Benzo[e]pyrene	$C_{20}H_{12}$										< 0.01%			

[a] Yields in part per million based on the original polymer weight

[b] Yields are based on the total volatiles recovered

[c] Based on the weight of the original polymer sample dried soot. Values increased with increasing sample size

[d] Based on the weight of the original polymer sample

[e] [illegible] present but not quantitated here

Table 6-3

POLYETHYLENE COMBUSTION AT 500 TO 1000°C

Product	Formula	Temperature Dependence of Product Yield: 500-560°C (20)	800°C (14)	850°C (23)	850-900°C (10)	900°C (21)	950°C (10)	1000°C (21)[c]	Nonflaming Combustion (29)	Flaming Combustion (29)
Weight loss	-									
Residue/char	-									
Total volatiles recovered	-									
Smoke	-		Increased with $[O_2]$						1 wt%[d]	0 65%[d]
Extractable organics in smoke	-								750 ppm[d] (45 ppm PAH)	75 ppm[d] (25 ppm PAH)
Soot	-			5 5-8 6%		~ 9-22%				
Carbon monoxide	CO							Major		
Carbon dioxide	CO_2									
Water	H_2O									
Low molecular-weight alcohols	ROH									
Ethanol	C_2H_5OH									
Cyclic ethers	-									
Furan	C_4H_4O									
Tetrahydrofuran	C_4H_8O									
Epoxy compounds	-									
Formaldehyde	HCHO	✓								
Aldehydes	RCHO				None					
Acetaldehyde	CH_3CHO									
Propionaldehyde	CH_3CH_2CHO									
Acrolein	CH_2 CHCHO	Trace								
Isobutyraldehyde	C_4H_8O									
n-Butyraldehyde	$CH_3CH_2CH_2CHO$									
Hexanal	$CH_3(CH_2)_4CHO$									
C_3-C_5 saturated and unsaturated aldehydes	-									
C_3-C_{12} aldehydes	-									
C_3-C_{18} aldehydes										
Ketones	RCOR'				None					
Acetone	CH_3COCH_3	Decreased with temp								
Methyl vinyl ketone	CH_3COCH CH_2									
Methyl propyl ketone	$CH_3COCH_2CH_2CH_3$									
Hexanone	$C_6H_{12}O$									
Octanone/C_5 ketone	$C_8H_{16}O$							Major		
Carboxylic acids	RCO_2H							Major		
Formic acid	HCO_2H				None					
Acetic acid	CH_3CO_2H	Only RCO 's								
Propionic acid	$CH_3CH_2CO_2H$									
Acrylic acid	CH_2 $CHCO_2H$									

(continued)

Table 6-3 (continued)

Product	Formula	Temperature Dependence of Product Yield: 500–550°C (20)	550°C (14)	600°C (22)[b]	550–650°C (10)[a]	600°C (23)[b]	950°C (14)[a]	1000°C (21)[c]	Nonflaming Combustion (25)	Flaming Combustion (49)
Crotonic acid	$CH_3CH{=}CHCO_2H$									
Hydroxy carboxylic acids	-									
Hydroxyisovaleric acid (hydroxy-3 methylbutanoic acid)	$C_5H_{10}O_3$									
Lactones (cyclic esters)	-									
Butyrolactone	$C_4H_6O_2$									
Valerolactone	$C_5H_8O_2$									
Paraffins (alkanes, aliphatic/saturated hydrocarbons)	C_nH_{2n+2}							Major		
Short-chain paraffins	C_nH_{2n+2}				✓					
Methane	CH_4									
Ethane	C_2H_6									
Cyclic alkanes	C_nH_{2n}									
Cyclopropane	C_3H_6									
Olefins (hydrocarbons unsaturated by one or more double bonds)	-									
α-olefins (-alkenes)	C_nH_{2n}				✓	✓		Major		
Ethylene	C_2H_4									
1-Pentene	C_5H_{10}									
1-Hexene	C_6H_{12}									
α,ω-olefins (-dienes)	C_nH_{2n-2}	More at 600°C			✓	✓				
Cyclic alkenes	C_nH_{2n-2}									
Long-chain α-olefins	-				✓					
Short-chain dienes	C_nH_{2n-2}				✓					
Two unidentified isomers	C_nH_{n-6}				✓					
C_{11}–C_{24} hydrocarbon liquid residue	-									
Benzene	C_6H_6	Increased with temp						Intermediate		
Toluene	$CH_3C_6H_5$	Increased with temp						Minor		
Ethylbenzene	$C_2H_5C_6H_5$							Intermediate		
Xylenes	$C_6H_4(CH_3)_2$									
Styrene	$C_6H_5CH{=}CH_2$							Intermediate		
Ethynylbenzene	$C_6H_5C{\equiv}CH$							Intermediate		
Biphenyl	$C_6H_5{-}C_6H_5$						< 1%			
Indan	C_9H_{10}				✓					
Indene	C_9H_8				✓		1.6%			
Naphthalene	$C_{10}H_8$				✓		1.5%			

Table 6-3 (continued)

Product	Formula	Temperature Dependence of Product Yield							Nonflaming Combustion (29)	Flaming Combustion (29)
		580-800°C (29)	800°C (19)	800°C[a] (22)	800-900°C (10)	900°C[b] (22)	950°C[b] (35)	1000°C[c] (21)		
1-Methylnaphthalene	CH_3-$C_{10}H_7$				/		? 0.1%			
2-Methylnaphthalene	CH_3-$C_{10}H_7$						1.2%			
2-Phenylnaphthalene	C_6H_5-$C_{10}H_7$						< 1%			
Acenaphthylene	$C_{12}H_8$						1.92%			
Fluorene	$C_{13}H_{10}$						< 1%			
9-Methylfluorene	CH_3-$C_{13}H_9$						< 1%			
Phenanthrene	$C_{14}H_{10}$						1.56%		48.16%[f] $C_{14}H_{10}$	12.47%[f] $C_{14}H_{10}$
4,5-Methylenephenanthrene	$C_{15}H_{10}$									2.45%[f]
Methyl-4,5-methylenephenanthrene	$C_{16}H_{12}$									0.61%[f]
Methylphenanthrene	$CH_3C_{14}H_9$									0.64%[f]
Anthracene	$C_{14}H_{10}$					~ 0.1%			48.16%[f] $C_{14}H_{10}$	12.47%[f] $C_{14}H_{10}$
Dihydroanthracene	$C_{14}H_{12}$						< 1%			
Fluoranthene	$C_{16}H_{10}$					~ 0.1%	< 1%			10.90%[f]
Pyrene	$C_{16}H_{10}$					~ 0.1%	< 1%		51.84%[e]	46.36%[f]
Methylpyrene	$C_{17}H_{12}$									1.14%[f]
Benzanthracene (or triphenylene)	$C_{18}H_{12}$									0.59%[f] $C_{18}H_{12}$
Benzo[c]phenanthrene	$C_{18}H_{12}$						< 1%			
2,3-Benzofluorene	$C_{17}H_{12}$									1.33%[f]
1,2-Benzofluorene	$C_{17}H_{12}$									1.77%[f]
Chrysene	$C_{18}H_{12}$					~ 0.1%	< 1%			0.59%[f] $C_{18}H_{12}$
2,13-Benzofluoranthene	$C_{20}H_{12}$									5.64%[f]
Benzo[a]pyrene	$C_{20}H_{12}$			0.05-0.06%		0.1-0.15% [0.06% in soot]	< 1%			
Benzo[e]pyrene	$C_{20}H_{12}$					~ 0.1%				

[a] Based on the weight of the original polymer sample, dried soot. Values increased with increasing sample size.

[b] Yield based on weight of cold trapped combustion products. The amount of the latter relative to the initial polyethylene sample was not given.

[c] Yields are based on the total volatiles recovered.

[d] Based on the weight of the original polymer sample.

[e] / = present but not quantitated.

[f] Mole percent based on the PAHs in the extractable organics from the soot.

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POLY(ETHYLENE TEREPHTHALATE) (MYLAR)

CASRN. 25038-59-9

Synonyms PET

Trade Names (producers) Mylar, Cronar (DuPont), Celanar (Celanese), Estar (Eastman Kodak), Scotchpar (3M); Videne (Goodyear), Avistar (FMC) (1) Products

with carboxy end groups are Dacron, Amilar, and Fiber V Products with methyl ester end groups include Terylene, Diolen, Enkalene, Fortrel, Tergal, Terital, Terlenka, Trevira, and Mylar (2).

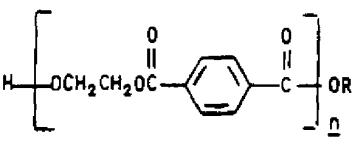
General Information

Molecular Formula: $(C_{10}H_8O_4)_n$

Structure of Monomers and Polymer:

Ethylene glycol

Terephthalic acid (R = H)
Dimethyl terephthalate (R = Me)



where R = H or CH_3

Poly(ethylene terephthalate)

Uses: Major markets for polyester films in 1966 included magnetic tape, electrical, packaging, and photography (1). Poly(ethylene terephthalate) (PET) is the most widely used film for electrical insulation (3). Electrical applications were second only to magnetic tape use in 1966. Polyesters are used for wire and cable insulation, transformer insulation, and in capacitors. Type A Mylar film, which has been biaxially structured and heat set, has numerous electrical uses such as slot liners, wedges, and phase insulation for motor and field coils, magnet wire insulation; a barrier and insulation tape in cables, transformer coil insulation, and backing for mica. Type C Mylar is used as a dielectric in high-temperature capacitors (1).

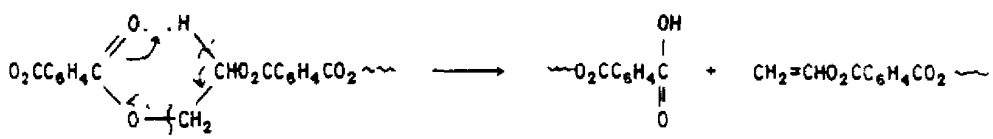
Glass-reinforced PET is the only thermoplastic recognized by Underwriters Laboratory for Class H (180°C) systems Class B (130°C) and Class F (155°C) systems may also use PET Many types of coil bobbins, including Class A transformer ballasts, are made from reinforced PET (4).

Thermal Decomposition Mechanisms

Pyrolysis and combustion of PET give similar products and similar product yields Thus, the mechanisms will not be discussed separately This discussion is based on four reviews published from 1970 to 1984 (5-8)

Degradation of PET under burning conditions is primarily pyrolytic rather than thermooxidative. For most of the decomposition, chain scission is rate limiting, with the secondary breakdown to small, volatile molecules being faster.

The predominant mechanism for chain scission involves proton transfer in a cyclic transition state:

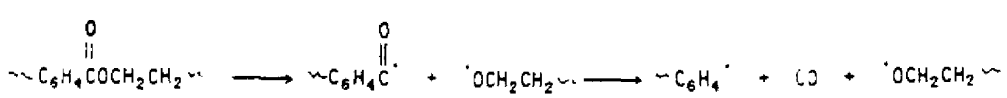


Random scission of the ester links gives rise to formation of vinyl ester oligomers. Scission close to the chain ends will give terephthalic acid, divinyl terephthelate, and vinyl terephthalic acid monoester ($CH_2{=}CHO_2CC_6H_4CO_2H$)

Decarboxylation of vinyl terephthalic acid monoester will give vinyl benzoate and CO_2; decarboxylation of terephthalic acid will give benzoic acid and CO_2; and decarboxylation of benzoic acid will give benzene and CO_2. Benzene production is not affected by the presence of oxygen. Benzoic acid, divinyl terephthalate, and vinyl benzoate yields decrease above aoout 700°C due to decomposition. The yield of vinyl benzoate is somewhat higher in the presence of oxygen, but yields of benzoic acid and divinyl terephthalate have higher yields from pyrolysis.

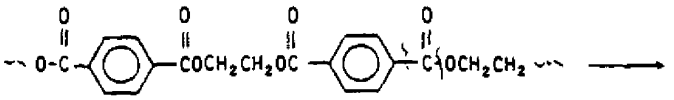
Both CO and CO_2 arise from decarboxylation following chain scission reactions, but evolution of CO_2 from PET on pyrolysis decreases somewhat above about 700°C Apparently CO_2 reacts with C above about 700°C to give more CO.

A likely route for CO production involves scission of the single bond between oxygen and the carbonyl carbon:

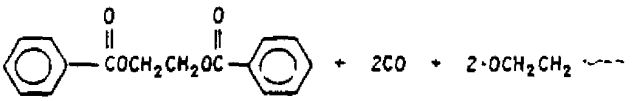


At higher pyrolysis temperatures, about as much CO is formed from this process as is CO_2 from the cyclic scission and decarboxylation reactions described above

On a weight percentage basis, ethylene dibenzoate is a significant thermal decomposition product although on a molar basis, its loss is not large More is lost from pyrolysis than from combustion. We conjecture that it may be formed in the scission reactions producing carbon monoxide.

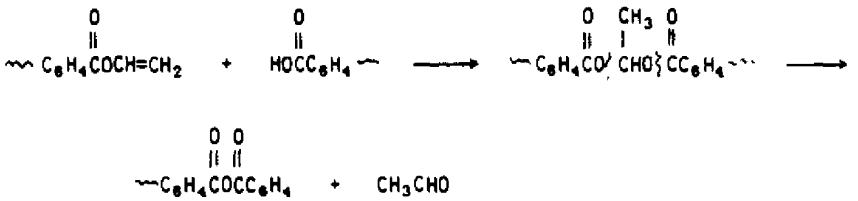


PET



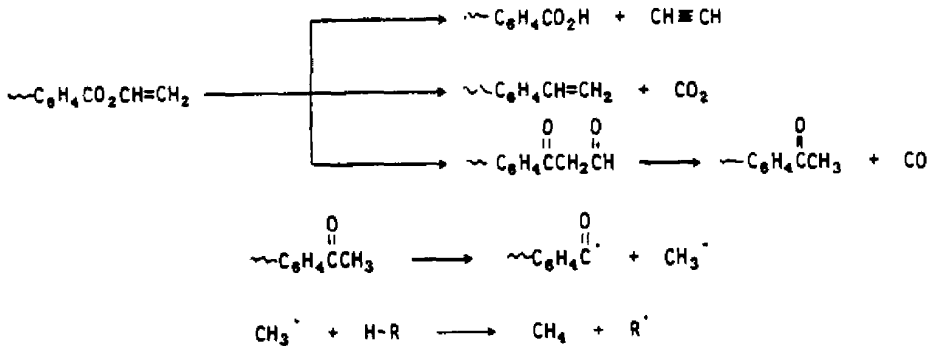
Ethylene dibenzoate

Formation of volatile acetaldehyde and of the anhydride species detected in nonvolatile char residues may be accounted for by the following scheme:



Acetaldehyde yields are similar during combustion or pyrolysis and decrease above about 600°C.

Methane and acetylene appear to be produced from very similar reactions in air or in its absence Reactions proposed that would lead to acetylene and methane formation are the following:



These reactions would also account for styrene and acetophenone Secondary decomposition of acetaldehyde may also account for methane and carbon monoxide

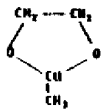
Summary of Experimental Studies Reviewed

Pyrolysis. Major products (in yields generally greater than about 10 weight percent based on the original polymer weight) from PET pyrolysis within the temperature range 288°C to about 700°C included acetaldehyde, carbon dioxide, divinyl terephthalate, vinyl benzoate, ethylene dibenzoate, and benzoic acid. Products formed in 1 to 9% yield included carbon monoxide, ethylene, acetylene, and benzene Trace to minor amounts of alcohols, aldehydes, ketones, benzene derivatives, acetylene, C_1 to C_3 alkenes or alkanes, and 2-methyl-1,3-dioxolane (the cyclic acetal formed from acetaldehyde and ethylene glycol, see Table 6-4 for structure) were also detected. Table 6-4 summarizes the pyrolysis experiments reviewed.

Combustion. Thermal oxidation or combustion of PET in the range 340 to about 730°C produced major amounts of carbon monoxide, carbon dioxide, acetaldehyde, acetylene, and PET dimers and trimers. Intermediate amounts of methane, vinyl benzoate, divinyl terephthalate, and benzoic acid were also reported. Less important products included tetramers, pentamers, formaldehyde, lower carboxylic acids, ethylene dibenzoate, benzene, terephthalic acid, and hydroxyethyl terephthalate monoester Results are summarized in Table 6-5.

Table 6-4

POLY(ETHYLENE TEREPHTHALATE) PYROLYSIS

Products	Formula	280°C[a] (9)	282-327°C (9)	300-400°C (10)	~ 500°C 10 sec (11)	581-625°C (12)	~ 700°C 10 sec (11)	~ 700°C 10 sec (6)
Weight loss					21 1%		89 8%	
Solid residue/char				Probably crosslinked char				
Carbon monoxide	CO	8%			4 59%		7 68%	Major
Carbon dioxide	CO_2	8 7%			10 40%		11 89%	Intermediate
Water	H_2O							Trace
Methane	CH_4	0 4%			0 89%		0 28%	
Acetylene	C_2H_2				2 81%		2 45%	Minor
Ethylene	C_2H_4	2 6%						Minor
C_1 - C_3 alkanes/alkenes	-						✓	Traces to minor
Ethylene glycol	$HOCH_2CH_2OH$					Minor		
Alcohols	ROH		✓					Minor
Acetaldehyde	CH_3CHO	80%			12 51%	Major	4 11%	Minor
Aldehydes	RCHO		✓					
Ketones	RCOR'						✓	Minor
2-Methyl 1 3 dioxolane		0 4%				Minor		
Benzaldehyde	C_6H_5CHO							Very minor
Benzoic acid	$C_6H_5CO_2H$				0 18%	Minor	16 06%	Major
Ethylene dibenzoate	$C_6H_5CO_2CH_2CH_2O_2CC_6H_5$		✓		10 65%		3 49%	Minor
Vinyl benzoate	$C_6H_5CO_2CH{=}CH_2$				9 96%		14 33%	Intermediate
Hydroxyethyl benzoate	$C_6H_5CO_2CH_2CH_2OH$					Minor		
Benzoates	$C_6H_5CO_2R$						✓	Minor
Divinyl terephthalate	$CH_2{=}CHO_2CC_6H_4CO_2CH{=}CH_2$				16 45%		15 77%	Minor
Terephthalates	$C_6H_4(CO_2R)_2$							Minor
Aromatic acids	$ArCO_2H$		✓					Minor
Benzene	C_6H_6	0 4%			0 22%		3 50%	Intermediate
Toluene	$C_6H_5CH_3$						✓	Minor
Ethylbenzene	$C_6H_5C_2H_5$							Minor
Styrene	$C_6H_5CH{=}CH_2$						✓	Minor
p Vinyltoluene	$CH_3C_6H_4CH{=}CH_2$							Very minor
Biphenyl	$C_6H_5{-}C_6H_5$							Minor
Acetophenone	$C_6H_5COCH_3$					Minor		Minor

[a] Yields based on percent of total volatiles.

Table 6-5

POLY(ETHYLENE TEREPHTHALATE) COMBUSTION

Product	Formula	340°C [11]	350°C [11]	400°C [15]	600°C [8]	≤ 500°C 2-3 min [16]	~ 510°C, 10 sec [7]	400-600°C [13]	~ 610°C, 10 sec [7]	~ 670°C, 10 sec [7]	~ 730°C, 10 sec [7]
Weight loss						50-80%	~ 30%				< 90%
Solid residue/char						Anhydride groups dominant					
Carbon monoxide	CO				Major		~ 15 moles		~ 50 moles	~ 65 moles	85 moles
Carbon dioxide	CO_2			✓			~ 25 moles		~ 70 moles	~ 60 moles	~ 60 moles
Methane	CH_4				Major				trace	~ 6 moles	~ 8 moles
Acetylene	C_2H_2						~ 10 moles		~ 27 moles	~ 29 moles	35 moles
Ethylene	C_2H_4										
Formaldehyde	HCHO	Max. amt in range 200-600°C									
Acetaldehyde	CH_3CHO				Major		~ 20 moles		~ 30 moles	~ 20 moles	10 moles
Acrolein	CH_2 CHCHO							trace			
Lower carboxylic acids	RCO_2H	Max. amt in range 200-600°C									
Terephthalic acid	$C_6H_4(CO_2H)_2$		✓	✓							
Benzoic acid	$C_6H_5CO_2H$			✓			~ 3 moles		~ 4 moles	~ 13 moles	8-9 moles
Hydroxyethyl terephthalate monoester	$HOCH_2CH_2O_2CC_6H_4CO_2H$		✓	✓							
Divinyl terephthalate	$C_6H_4(CO_2CH{=}CH_2)$						~ 4 moles		~ 10 moles	~ 10 moles	~ 6 moles
Vinyl benzoate	$C_6H_5CO_2CH{=}CH_2$						~ 3 moles		~ 18 moles	~ 14 moles	~ 12 moles
Ethylene dibenzoate	$C_6H_5CO_2CH_2CH_2O_2CC_6H_5$						~ 1 mole		~ 2.8 moles	~ 2.5 moles	~ 1 mole
Dimers			Major	✓							
Trimers			Major	✓							
Tetramers			✓	✓							
Pentamers			✓								
Benzene	C_6H_6						trace		2 moles	~ 3.5 moles	8 moles

[a] Polymer had ~ 100 repeating units

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POLYSTYRENE

CASRN. 9003-53-6

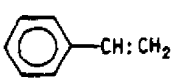
Synonyms. Styrene polymer; Vinylbenzene polymer, Ethenylbenzene homopolymer

Trade Names (producers). Styron 666 U (Dow); Lustrex PIX6 (Monsanto, UK); Dylene, Trycite, Hostyren (American Hoechst); Styrofoam (Dow). [There are more than 100 others.]

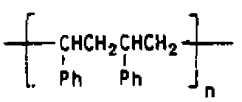
General Information

Molecular Formula: $(C_6H_5CHCH_2)_n$

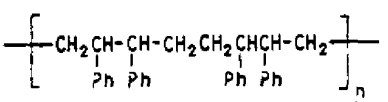
Structure of Monomer and Polymer:



Styrene



head-to-tail



head-to-head-tail-to-tail

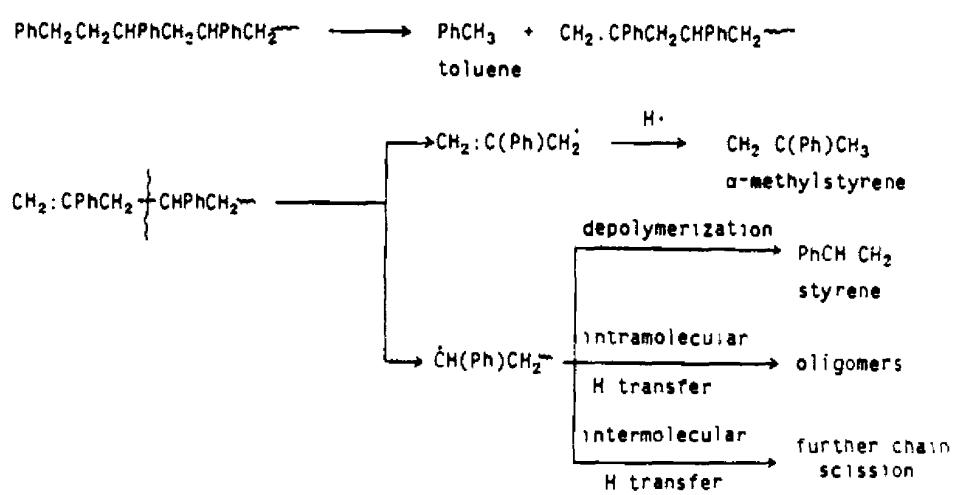
Uses: Electrical equipment; packaging; refrigerator doors, air conditioner cases, containers and molded household wares; machine housings, toys, clock and radio cabinets. Foams are used for thermal insulation, light construction (e g , boats), ice buckets, water coolers, fillers in shipping containers, furniture construction Spheres are used as a radiator leak stopper (1) Ignition-resistant grades, which include halogenated organic compounds and antimony oxide, may be used in appliances, business machines, and electronic parts. Impact grades, which have improved resistance to hydrocarbon solvents, are acceptable for containers of food products containing fats and oils. Polystyrene use in magnetic tape cassettes, reels, and other consumer electronic components is a growth market (2).

Thermal Decomposition Mechanisms

Above ~ 330°C, polystyrene degrades by the following reactions

- Chain-end initiation
- Random scission of "weak links" (does not directly give volatiles below ~ 440°C)
- Depolymerization (unzipping) to give monomer.
- Intramolecular transfers to give dimers, trimers, and higher oligomers.
- Intermolecular transfer to give short-chain fragments

The mechanism of polystyrene thermal degradation is still being actively studied (3). Scission by a radical process of C-C bonds β to chain end unsaturations must be preceded by reactions that create these unsaturations Thus, the first step is removal of benzylic end units as shown (4):



Since the concentration of unsaturated chain ends increases throughout the degradation, formation of volatiles from depolymerization is accelerated Regardless of the initial molecular weight of the polystyrene (≥ 4000), the ratio of the rates of weight loss and α-methylstyrene evolution is constant throughout the degradation. Since the rate of toluene formation tends to increase throughout degradation, toluene must originate from other reactions besides the initial cleavage of the benzylic end groups One of the sources is the newly created

benzylic end groups formed from the β scissions. Other mechanisms have also been proposed (5).

Volatiles include mainly styrene and styrene dimer with other volatile oligomers Short-chain fragments comprise an oily, high-boiling product. The solid residue comprises a lower molecular weight polymer than the original Other aromatic hydrocarbons identified in the degradation products are benzene, toluene, ethylbenzene, isopropylbenzene, n-propylbenzene, allylbenzene, and α-methylstyrene (3)

Three distinct patterns of chain scission occur at subvolatilization temperature (280 to 300°C in vacuo) (6):

1. If the polystyrene was prepared anionically, chain scission is simple and random with the degree of degradation directly proportional to the heating time.
2. For polystyrenes polymerized thermally, very rapid scission of a small number of "weak links" occurs, after which the degree of degradation is again proportional to the heating time.
3. Polystyrenes whose polymerization was initiated by free radicals degrade by three processes having different rates:

   (a) Scission of highly labile "weak links."

   (b) Scission of fairly weak bonds.

   (c) "Normal" bond scission.

Processing polystyrene in the presence of air gives groups capable of absorbing ultraviolet radiation, presumably hydroperoxy groups, which decompose to form ketone groups (7):

$$\sim\sim CH_2C(Ph)(OOH)CH_2CH(Ph)\sim\sim \xrightarrow{UV}$$

$$\sim\sim CH_2C(:O)Ph + H_2O + PhCH:CH\sim\sim$$

Summary of Experimental Studies Reviewed

So much work has been done on the pyrolysis and combustion of polystyrene that only references from the last 5 years were surveyed.

Pyrolysis. Styrene is usually reported as a major pyrolysis product (40 to 90% of volatiles) throughout the temperature ranges used in the studies reviewed (60 to 1400°C) (8-19). Using ultrathin film samples, Lehrle et al (1982) (11) found monomer was the only polystyrene degradation product from pyrolysis at 450 to 480°C. Toluene, α-methylstyrene, cumene (isopropylbenzene), dimer (2,4-diphenyl-1-butene), and trimer (2,4,6-triphenyl-1-hexene) are frequently reported (12-15). Schroeder et al (1984) (16) identified a triphenylbenzene after pyrolysis at 292 to 336°C. Toluene represents 6% of the volatiles at 510°C (17); α-methylstyrene is a major product at 700°C (12), dimer and trimer have been reported as major products at 300, 348, and 900°C (12,13,18). Most of the remaining products that have been tentatively identified (~ 100) are mono- through hexaphenyl-substituted oligomer chains containing 2 to 14 carbons in the chain and usually some unsaturation. Triphenyl- and tetraphenyl-substituted C_9 and C_{10} chains were identified as major products at 700°C, and many other products were found in yields surpassing those of toluene and styrene. Relative amounts of pyrolysis products are difficult to judge from the results published by Lai and Locke (1984) (12).

In contrast to the results of Lai and Locke (1984) (12), who found numerous products of the type (poly)phenyl-substituted chains by GC/MS, Smith (1984) (19) reported that at 700°C, only styrene and α-methylstryene were major products, toluene was formed in intermediate yield, and the minor products were hydrocarbons given as formulas with four to eight carbons and with only one or two unsaturations. Irwin (1982) (20) reviewed several other pyrolysis studies indicating that the variation in the product distribution was largely due to the techniques used to pyrolyze the polystyrene sample. The temperatures, however, were not indicated for any of the experiments reviewed.

Only two groups (17,18) reported finding any polycyclic aromatic hydrocarbons (indene, methylindene, and methylnaphthalene) and these identifications were only tentative.

Combustion. Processing polystyrene in air (injection molding, thermoforming, or thermocutting; temperatures not given) produced workplace styrene concentrations ~ 0.1 to ~ 1.0 mg/m³ air (well below the OSHA permissible exposure limit of 100 mg/m³), polymer fume concentrations < 0.5 to > 1.0 mg/m³, and total aldehydes ~ 0.1 to ~ 0.3 mg/m³. Depending on the operation, concentrations of ~ 0.1 to ~ 0.3 mg/m³ formaldehyde, acetaldehyde, formic acid, and acetic acid may be generated. Other oxidized products included benzaldehyde (C_6H_5CHO), benzoic acid ($C_6H_5CO_2H$), and acetophenone ($C_6H_5COC_6H_5$) (Valmiotalo, unpublished data).

Pfäffli, 1984) (3) Major products detected in the liquid residue from polystyrene degradation starting at about 300°C and ending with complete combustion at about 450°C were styrene, phenol, and toluene. Other products identified were ethylbenzene, benzaldehyde, two methylstyrenes, n-propylbenzene, indene, methylindene, acetophenone, naphthalene, methylnaphthalene, cinnamyl alcohol, biphenyl or acenaphthene, methylbiphenyl, and diphenylethane (21).

Benzaldehyde, phenylacetaldehyde ($C_6H_5CH_2CHO$), and other aldehydes were detected along with benzene, toluene, ethylbenzene, styrene, and propylbenzene when flame-retarded polystyrene was combusted at temperatures up to 490°C (Masarik et al , 1976; cited by Hawley-Fedder et al., 1984) (22). The flash-ignition temperature of polystyrene is 345 to 360°C, the self-ignition temperature is 490°C (23) Morikawa (1978, cited by Hawley-Fedder et al , 1984) (22) subjected polystyrene to flaming combustion at 600 to 900°C. A soot containing polycyclic aromatic hydrocarbons (PAHs) was obtained in 50% yield based on the initial polymer weight Most of the PAHs were generally 3- and 4-membered-ring species Hawley-Fedder et al (1984) (22) trapped and identified > 100 products, mostly PAHs, after combusting polystyrene at 800 to 950°C. At 950°C, indene, naphthalene, biphenyl, and phenanthrene were the major products along with 29 others. Below 950°C, there were eight major peaks in the total ion chromatogram produced by capillary gas chromatography-mass spectrometry. Besides the four PAHs mentioned at 950°C, methylstyrene, (p-methylphenyl)phenylacetylene ($CH_3C_6H_5C_6H_5C{:}CH$), and 1- and 2-methylnaphthalene were the major products Another 40 to 50 compounds were identified. Among the PAHs identified were fluorene and substituted fluorenes, substituted phenanthrenes and anthracenes, fluoroanthene, benzo[j,k]fluoranthene, benzo[e]pyrene, 3-methylcholanthene, pyrene, benzo[a]fluorene, benzo[b]fluorene, benzo[g,h,i]perylene, benzo[c]phenanthrene, benz[a]anthracene, and chrysene

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MONS 020538

Appendix A

SUMMARY OF UTILITY MATERIALS PROPOSED FOR EXPERIMENTAL TESTING
AND THEIR TOXIC THERMAL DEGRADATION PRODUCTS

This appendix lists the utility industry materials that have been proposed for EPRI-sponsored review and/or experimental testing. Most of the materials were listed in the Request for Proposal for the current project. Additional materials such as Nomex and many of the polymeric coating materials were suggested after initiation of the project.

In the column "Literature Reviewed," an S indicates that the material's thermal degradation was reviewed in a recent EPRI report by SCS Engineers, Inc (1) An M indicates the materials reviewed by MRI in the text of the present report. The most toxic thermal degradation products (other than carbon monoxide) that have been reported in the literature or that could be presumed to be formed based on the elemental composition or substructural components of the materials are given in the table. Where MRI or SCS Engineers (1) has reviewed the materials, the products are primarily those listed in these reviews For other materials, one or more reference citations are given for the known thermal degradation products listed. The products listed in these cases are based on a brief examination of the literature MRI has collected on the unreviewed materials. (For most of these materials, the literature search and acquisition was as comprehensive as that for the materials reviewed in this report.)

Material Name	Molecular formula	Literature Reviewed	Material Toxicity[b]	Likely to Produce Harmful Pesticides from a Fire[c,d]	Low Volatility Compounds Reported in Literature[e]	Highly Toxic Volatiles Other than CO
Polymers						
Bisphenol epoxy	$(C_{19}H_{20}O_3)_n$, cured may contain N	M	?? (uncured) (3)	PAHs	Naphthalene, styrene, cresols	Phenols, toluene, benzene, methyl chloride, acetaldehyde
Cellulose filled phenolic	C,H,O	D		PAHs		
Chlorosulfonated polyethylene (Hypalon 48)	C,H,Cl,O,S	M		PAH	PAHs	HCl, toluene, benzene, SO_2
Crosslinked polyethylene	C,H,(O),(Si)	M		PAHs	Phenol, char	Benzene, chloroform, toluene
Formvar	C,H,O	D				
Glass fiber-reinforced resins	(Numerous resins used)	-				
Melamine formaldehyde resin	C,H,N,O	-		PAHs, PAH		NH_3, HCN (4)
Nomex aramid	$(C_{14}H_{10}N_2O_2)_n$	M--		PAHs, PAH	Phenol, xylidine, aniline, hexanitrile	HCN, N_2O, NO, NH_3, cyanogen, acetonitrile, acetaldehyde, acetic acid, benzene, toluene, dioxane
Nylons (e.g., Nylon 6)	$(C_6H_{11}NO)_n$	M		PAH, PAHs	Oligomers	HCN, NH_3, nitriles, monomers, olefins
Phenolic resins (usually phenol HCHO)	C,H,O	--		PAHs, PAH	Acenaphthylene, naphthalene, cresol, phenols, styrene, black opaque residue and unknown, avg mol wt 340 (3-4 benzene rings), char (5-7)	Benzene, toluene, alcohols, HCHO, benzoic acid (5-7)
Polybutadiene	$(C_4H_6)_n$	-		PAHs	Wax-like material (avg mol wt 239, oligomers (6,8)	Benzene (6)
Polyesters (see also Mylar under films)	C,H,O	--		PAHs	PAHs	Aldehydes, ketones, aromatics (9)
Polyethylene	$(CH_2CH_2)_n$	M--		PAHs	Acrylic acid, butyric acid, naphthalene, chrysene, benzo[a]pyrene, other PAHs	Acrolein, formaldehyde, acetaldehyde, butyraldehyde, isobutyraldehyde, valeraldehyde, formic acid, acetic acid, benzene, toluene, ethyl alcohol, furan, tetrahydrofuran
Polystyrene	$(C_8H_8)_n$	M--		PAHs	Oligomers, PAH	Styrene, HCHO, benzene, acetaldehyde, toluene, formic acid, acetic acid

Material Name	Molecular formula	Literature Reviewed[a]	Material Toxicity[b]	Likely to Produce Harmful Residuals from a Fire[c]	Low Volatility Compounds Reported in Literature	Highly Toxic Volatiles Other than CO
Polysulfone (copolymer of bisphenol A and 4,4'-dichlorodiphenyl sulfone)	$(C_{27}H_{28}SO_4)_n$	H[1]		PAH, PANs	Styrene, uncharacterized residue	SO_2, benzene, toluene
Polyurethanes	C H N O	H[1]		PAH, PANs	PANs, quinoline	Aldehydes, HCN, nitriles, benzene
Poly(vinyl chloride)	$(CH_2CHCl)_n$	S[1]		CDD, CDF	Styrene, BCA, o p, chlorinated benzenes and PCBs, char, naphthalene, benz[a]pyrene and other PAHs	HCl, benzene, toluene, phosgene, vinyl chloride
Poly(vinylidene chloride)	$(CH_2CCl_2)_n$	+		PANs	Saran carbon (graphite in amorphous carbon) ([10])	HCl, traces of benzene, vinyl chloride, toluene, vinylidene chloride, chlorinated benzenes ([11,12])
Poly(vinylidene fluoride)	$(CH_2CF_2)_n$	+			Oligomers, fluorinated aromatics, usable material, black residue ([13,14])	HF
Teflon	$(C_2F_4)_n$	H[1]			Degraded polymer particulate	CF_4, COF_2, F^- + glass - SiF_4
Teflon FEP	$(C_3F_6)_n$	H[1]				
Teflon PFA	C H F O	H			Degraded polymer particulate	
Tefzel (tetrafluoroethylene ethylene copolymer)	$(C_2H_4F_4)_n$	H[1]		PANs		HF, COF_2, vinylidene fluoride
Rubbers						
Butyl rubber	97% $(C_4H_8)_n$ 3% $(C_5H_{10})_n$	+		PANs		1,3-Butadiene, 4-vinylcyclohexene ([15,16])
Ethylene propylene rubber	$(C_5H_{10})_n$			PANs		No highly toxic products reported among numerous alkanes and alkenes ([17,18])
Neoprene (polychloroprene)	$(C_4H_5Cl)_n$	H[1]		PANs	Long chain hydrocarbons	HCl, HCN, H_2S, SO_2
Nitrile rubber (acrylonitrile butadiene copolymers)	$(C_6H_7N)_n$	H[1]		PANs, PAH	Uncharacterized residue, oligomers	NH_3, HCN, acrylonitrite, other nitriles
Silicone rubber (e.g. polydimethylsiloxane)	$(C_2H_6OSi)_n$					
Viton (vinylidene fluoride hexafluoropropylene copolymer)	C H F	H[1]				Vinylidene fluoride, HF

Material Name	Molecular Formula	Literature Reviewed[a]	Material Toxicity[b]	Likely to Produce Harmful Residuals Upon Fire[c,d]	Low Volatility Compounds Reported in Literature[e]	Highly Toxic Volatiles Other Than CO
Adhesives						
Casein glue	C,H,N,O,S	0		PANs, PAH		
Hide glue	C,H,N,O,S	0		PANs, PAH		CH_3SCN,[d] pyrrole[d] (78)
Poly(vinyl butyral)	C,H,O	•		PANs		Acetaldehyde, butyraldehyde (ocean (23))
Films						
Halar (ethylene-chlorotrifluoroethylene copolymer)	$(C_4H_5ClF_3)_n$	H				HCl, HF, COF_2
Kapton (H film)	$(C_{22}H_{10}N_2O_5)_n$	H•		PANs, PAH	Phenol, highly conductive char	HCN, benzene, nitriles
Mylar [poly(ethylene terephthalate)]	$(C_{10}H_8O_4)_n$	H••		PANs	Benzoic acid, naphthalene, low oligomers, polyaromatic char	Acetaldehyde, formaldehyde, acrolein, benzene, styrene, toluene
Fluids						
Benzyl neocaprate (Paradol 100, discontinued)	$C_{17}H_{24}O_2$	SU	)7	PANs	Phenols[d]	Benzene[d]
Bis(2-ethylhexyl) phthalate (DEHP)	$C_{24}H_{38}O_4$	S•	0 2		OCA (in the presence of chlorinated substances), phthalic anhydride	
Butylated monochloro-diphenyl ether (Dielectric fluid C-4)	$C_{16}H_{17}ClO$	SU		mono-CDF (toxic?)	Phenol[d]	Benzene[d]
Formel NF [blend of perchloromethylene and Freons]	C,Cl,F	S•				Cl_2
Chlorohenzenes[g] (mono-, tri- and tetra)	C,H,Cl	S••	0-2		OCA, CDF, COD	HCl, vinyl chloride
Bl-n octyl phthalate	$C_{24}H_{38}O_4$	S•	o-2		OCA (in the presence of chlorinated substances), phthalic anhydride	
Freons	C,F Cl					
Freon (13	$C_2Cl_3F_3$	S•	22			Phosgene, Cl_2, COF_2, HF

Material Name	Molecular Formula	Literature Reviewed[a]	Material Toxicity[b]	Likely to Produce Harmful Residuals from a Fire[c]	Low Volatility Compounds Reported in Literature[e]	Highly Toxic Volatiles Other than CO
High molecular weight hydrocarbon liquids	C,H	•				No highly toxic products (H_2, acetylene, and other gaseous hydrocarbons (22)
Isopropylbiphenyl (Monsol)	$C_{15}H_{16}$	SO	I?	PAHs	Phenols[d]	Benzene,[d] toluene[d]
Methylated diphenylethane (1,1-diarylethane)	$C_{14}H_{14}$	SO	M I	PAHs	Phenols[d]	Benzene,[d] toluene[d]
Mildel (pentaerythritol aliphatic esters and aromatic triesters)	C,H,O	-		PAHs		Aldehydes, etc[d]
Mineral oil?	C,H	-		PAHs		No gaseous substances more toxic than CO (23)
Naphthenic oils	C,H	-		PAHs		Benzene, toluene (24)
PCBs (askarels, Aroclors)	C H Cl	••	3 (25)		CDD, CDF, OCA (26)	Chlorinated phenols[d]
Perchloroethylene (Wesocal transformer fluid)	C_2Cl_4	S•	2 (?)	Trichloroacetic acid		Cl_2, HCl, no phosgene, except perhaps from a revolding
Phenylxylylethane	$C_{16}H_{18}$	SO	I?	PAHs	Phenols[d]	Benzene,[d] toluene[d]
Propyldiphenyl	$C_{15}H_{16}$	SO	I?	PAHs	Phenols[d]	Benzene,[d] toluene[d]
Polyi-octene) (PAO 3)C()	C,H	S		PAHs		Aldehydes, alcohols, carboxylic acids
RTEmp (no aromatic content)	C,H	S-	07	PAHs		
Silicone[g] (polydimethyl siloxane)	$(C_2H_6OSi)_n$	S••			Naphthalene, styrene (27)	HCHO, HCO_2H H_2 benzene toluene (27)
Sulfur hexafluoride	SF_6	S••	02 I		Metal fluorides (arcing products in circuit breakers) (28)	SOF_2, SO_2, F_2, SOF_2, SF_4, S_2F_{10} SF_6
Paints and Other Coatings						
Acrylic lacquers	C H O,(N)	•		PAHs PAE	Styrene (29)	NH_3, HCN amines[d] (depends on particular polymer) acrolein benzene (29)
Coal tar epoxy	C H O	•				

Material Name	Molecular Formula	Literature Reviewed[a]	Material Toxicity[b]	Likely to Produce Harmful Residues from a Fire[c]	Low Volatility Compounds Reported in Literature[d]	Highly Toxic Volatiles Other Than CO
Epoxy resins and powders (see Bisphenol A epoxy resin under Polymers)	C,H,O					
Epoxy/urea formaldehyde resin	C,H,N,O	f				
Formex wire enamel		f				
Formvar® (polyvinyl formal and other resins)	C,H,O	-		PAHs		
Polyester powder (see Polyesters under Polymers and Mylar under Films)	C,H,O			PAHs		
Shellac (hydroxyl fatty acid derivatives)	C,H,O	-		PAHs	Fume and char (30)	
Urethane resins and powder (see Polyurethane under Polymers)	C,H,N,O			PAH, PAHs		
Varnished cambric	C,H,O	g				
Miscellaneous						
Acrylonitrile	C_3H_3N		3 (31)	PAH		HCN acetonitrile propionitrile, methacrylonitrile (32)
Cellulose insulation						
Dicyandiamide (dicy) treated paper	C,H,N,O	Mm				
Kraft board/paper	$(C_6H_{10}O_5)_n$	M			Levoglucosan, char	Acetylene and other hydrocarbons
Bag paper	C,H,O	f				
Creosote (contains PAH)	C,H	M		PAHs	Toluidine, xylidene, cresol, naphthalene, phenol, quinoline, benzo[a]pyrene many other PAHs, α- and β naphthylamine, aniline	
Pentachlorophenol[e]	C_6HCl_5O	M	3 (3)		CDD CDF	Hexachlorobenzene
Polysil (polymer-bonded silica)	C,Si	g				

[a] M = Discussed by MRI in this report
S = Discussed by SCS Engineers in March 1986 report (1)
If no M or S, MRI has briefly checked literature on hand
++ = Considerable literature information on both pyrolysis and combustion (1967 to the present)
+ = Some information found in the literature, but many gaps
- = Very little pertinent information found in the literature
0 = No pertinent information found in the literature

[b] Toxic hazard rating (Source: Toxicity Profiles of PCB Substitutes (2) unless otherwise noted. Information on toxicity of most of the materials was not readily available in secondary sources):
0 = No known toxic effects
1 = Slight and reversible toxicity
2 = Moderate toxicity, reversible or irreversible effects do not threaten life or result in serious physical impairment
3 = Severe toxicity, brief exposure or low doses threaten life or cause severe and irreversible impairment
a/ = A question mark by the rating indicates an assumption based on limited toxicological data
0 1 = No information to assign rating in reference 2
A range of ratings may be entered here because the reference gives separate ratings for acute and chronic exposure by route of exposure

[c] PAHs = polycyclic aromatic hydrocarbons
PCBs = Polychlorinated biphenyls
PAX = PAH analogs containing other atoms (O, N, S) substituting for carbon in one or more rings
CDD = Polychlorinated dibenzo-p-dioxins or analogs
CDF = Polychlorinated dibenzofurans or analogs
OCA = Other chlorinated aromatics

[d] Speculative products based on composition

[e] EPRI sponsored experimental work has been done or is in progress

[f] Samples have been supplied but no literature search was done

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Appendix 8

HEALTH AND SAFETY INFORMATION FOR THERMAL DEGRADATION PRODUCTS

INTRODUCTION

This appendix summarizes health and safety information for the products released by thermal degradation or volatilization from several materials used in the electric power industry. Besides health and safety information, the physical state of each product at room temperature and pressure is indicated. Solids and semivolatile liquids would require greater decontamination effort after a fire involving these materials than would the gaseous and volatile liquid products, which would largely dissipate during or immediately after a fire.

The appendix includes most of the products from thermal degradation of the materials reviewed in this document. The listing is not exhaustive because sometimes the degradation products were so numerous from certain materials that some products were grouped in this review as a member of a chemical compound class such as α-olefins or benzoate esters. Other products not specifically listed in the document and/or this appendix were high-molecular-weight trimers, tetramers, and higher oligomers.

To help the reader readily identify which degradation products came from each material reviewed, the materials are listed below with a mnemonic for each name. Following that list is a list with the mnemonics in alphabetical order.* The appropriate mnemonics appear in parentheses by the name of each product in the appendix.

Chlorosulfonated polyethylene	CSPE
Creosote**	CRE
Crosslinked polyethylene†	XLPE
Bisphenol A epoxy	EPO
Halar	HAL
Kapton	KAP
Kraft paper	PAP
Neoprene	NEO

*No products were found for thermal degradation of Teflon PFA, and there were no simple products to list for Nylon 11.
**In material itself and/or from thermal degradation products
†From additive

Nitrile rubber	NIT
Nomex	NOM
Nylon 6	NY6
Nylon 6,6	N66
Nylon 6,10	610
Pentachlorophenol	PCP
Polyethylene	PE
Poly(ethylene terephthalate) (Mylar)	PET
Polystyrene	STY
Polysulfone	SUL
Polyurethane	PU
Teflon	TEF
Teflon FEP	FEP
Tefzel	TFZ
Viton	VIT

610	Nylon 6,10
CRE	Creosote
CSPE	Chlorosulfonated polyethylene
EPO	Bisphenol A epoxy resin
FEP	Teflon FEP
HAL	Halar
KAP	Kapton
N66	Nylon 6,6
NEO	Neoprene
NIT	Nitrile rubber
NOM	Nomex
NY6	Nylon 6
PAP	Kraft paper
PCP	Pentachlorophenol
PE	Polyethylene
PET	Poly(ethylene terephthalate)
STY	Polystyrene
SUL	Polysulfone
PU	Polyurethane
TEF	Teflon
TFZ	Tefzel
VIT	Viton
XLPE	Crosslinked polyethylene

Two sources were used for the health and safety information, RTECS, Registry of Toxic Effects of Chemical Substances 1981-1982* (1) and the "Industrial Hygiene Technical Manual, Appendix A" (2). Information from the latter reference is usually more extensive and includes OSHA standards (limits) for exposure to the product in workplace air. Physical property information was derived from the Aldrich Catalog Handbook of Fine Chemicals 1986-1987, (3), the Merck Index (4), the Condensed Chemical Dictionary (5), or the CRC Handbook of Chemistry and Physics (6).

*Note: A 1983-1984 supplement has been published but was not used for this report

The Chemical Abstracts Service Registry Number (CASRN) follows most of the product names in the appendix The CASRN is a unique identifier that greatly facilitates computerized searches for compound-specific information in databases that routinely use CASRNs such as CA Search or CAS ONLINE We have included the CASRNs for those readers who wish to find more detailed information about particular products

EXPLANATION OF ABBREVIATIONS AND HEALTH CODES

CARC = Carcinogenic effects identified.

CASRN = Chemical Abstracts Service Registry Number.

DESC = Description. The physical state of a substance at standard temperature and pressure.

EYE IRR = Eye irritation.

H = Hours of exposure.

HLTH = Toxicological properties along with the eppropriate health code

IARC = International Agency for Research on Cancer.

IHL = Toxic dose from inhalation; value shows length of exposure.

ORAL or INGES ACUTE = Ingestion acute, toxic dose from short-term ingestion

INGES CHRONIC = Ingestion chronic.

IPR = Toxic dose from intraperitoneal administration.

IVN = Toxic dose from intravenous administration.

LC_{50} = Concentration in air required to kill half of the test animals

LD_{50} = Dose, in mg substance per kg body weight of the test animal, required to kill half of the test animals.

LD_{Lo} or TD_{Lo} = Lowest lethel dose or lowest toxic dose reported.

NTP = National Toxicology Program.

OSHA = Occupational Safety and Health Administration.

PAH = Polycyclic aromatic hydrocarbon.

SCU = Toxic dose from subcutaneous administration.

SKIN or SKIN ABS = Skin absorption, toxic from dermal exposure

SKIN IRR = Skin irritation.

MONS 020554

STDS = Standards: OSHA = Permissible exposure limit
TLV = ACGIH-threshold limit value
TWA = Time-weighted average
STEL = Short term exposure limit
Permissible exposure limits are those adopted by OSHA or recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) (1982 Threshold Limit Values TLVs® list)
A "C" indicates a ceiling limit of exposure

W = Weeks of exposure.

The health codes listed below describe the toxicological properties of the chemical substance.

Health Code	Health Effects
1	Cancer - Currently regulated by OSHA as a carcinogen
2	Chronic (Cumulative) Toxicity - Known or suspected animal or human carcinogen, mutagen (except Code No 1 chemicals)
3	Chronic (Cumulative) Toxicity - Long-term organ toxicity other than nervous, respiratory, hematologic, or reproductive
4	Acute Toxicity - Short-term high risk effects.
5	Reproductive Hazards - Teratogenesis or other reproductive impairment.
6	Nervous System Disturbances - Cholinesterase inhibition
7	Nervous System Disturbances - Nervous system effects other than narcosis.
8	Nervous System Disturbances - Narcosis
9	Respiratory Effects Other Than Irritation - Respiratory sensitization (asthma or other).
10	Respiratory Effects Other Than Irritation - Cumulative lung damage.
11	Respiratory Effects - Acute lung damage/edema or other
12	Hematologic (Blood) Disturbances - Anemias
13	Hematologic (Blood) Disturbances - Methemoglobinemia
14	Irritation-Eyes, Nose, Throat, Skin - Marked
15	Irritation-Eyes, Nose, Throat, Skin - Moderate
16	Irritation-Eyes, Nose, Throat, Skin - Mild
17	Asphyxiants, Anoxiants

18	Explosive, Flammable, Safety (No Adverse Effects Encountered When Good Housekeeping Practices are Followed).
19	Generally Low Risk Health Effects - Nuisance particulates, vapors, or gases
20	General Low Risk Health Effects - Odor.

MONS 020556

Acenaphthene [a PAH] (CRE, CSPE?, STY)
CASRN: 83-32-9
DESC: Solid, m.p. 93-95°C
MUTAGEN

Acenaphthylene [a PAH] (CRE, CSPE?)
CASRN: 208-96-8
DESC. Solid, m.p. 88-91°C
MUTAGEN

Acetaldehyde, Ethanal (NOM, PE, PET, PU, STY)
CASRN: 75-07-0
STDS: OSHA: 200 ppm, 360 mg/m³
TLV. 100 ppm, 180 mg/m³ TWA; 150 ppm, 270 mg/m³ STEL
DESC: Volatile Liquid
HLTH Irritation-Eyes, Nose, Throat, Skin--Marked (14).
Narcosis (8).
Kidney damage (3)
SKIN IRR: Mild
INGES ACUTE: Rat LD_{50}: 1930 mg/kg

Acetic acid; Ethanoic acid (NOM, PE, STY)
CASRN: 64-19-7
STDS: OSHA: 10 ppm, 25 mg/m³
TLV: 10 ppm, 25 mg/m³ TWA; 15 ppm, 37 mg/m³ STEL
DESC Volatile Liquid
HLTH. Irritation-Eyes, Nose, Throat, Skin--Marked (14, Greater than 30 ppm)
SKIN IRR: Yes (if concentrated)
INGES ACUTE: Human TD_{Lo}: 1.47 mg/kg

Acetone (EPO, NOM, PU)
CASRN: 67-64-1
STDS: OSHA: 1000 ppm, 2400 mg/m³
TLV: 750 ppm, 1780 mg/m³ TWA, 1000 ppm, 2375 mg/m³ STEL
DESC: Volatile Liquid
HLTH: Irritation-Eyes, Nose, Throat--Mild (16, Less than 2000 ppm).
Narcosis (8, Greater than 2000 ppm)
SKIN IRR Mild
INGES ACUTE: Rat LD_{50} 9750 mg/kg

Acetonitrile (NIT, NOM, PU)
CASRN: 75-05-8
STDS: OSHA: 40 ppm, 70 mg/m³
TLV: 40 ppm, 70 mg/m³ TWA; 60 ppm, 105 mg/m³ STEL
DESC: Volatile Liquid
HLTH: Irritation-Eyes, Nose, Throat--Mild (16, Less than 50 ppm)
Acute Toxicity (Cyanosis) (4, Greater than 50 ppm).
SKIN ABS: Yes
SKIN IRR: Yes
INGES ACUTE Human TD_{Lo}: 570 mg/kg

Acetophenone; Diphenyl ketone (PET, STY, XLPE)
CASRN: 98-86-2
DESC: Semivolatile Liquid (m.p. 19-20°C)
SKIN IRR. Rabbit: 515 mg, open, mild
ORAL: Rat LD_{50}: 900 mg/kg

Acetylene; Ethyne (EPO, NOM, PAP, PE, PET, PU)
CASRN: 74-86-2
DESC. Gas
HLTH: Explosive (18).
Asphyxiation (17, Greater than 2500 ppm)
ACGIH: E (Simple asphyxiant)

Acridine (CRE)
CASRN: 260-94-6
DESC: Solid, m.p. 107-110°C
SCU: Mouse LD_{50}: 400 mg/kg
IVN: Rabbit LD_{50}: 100 mg/kg

Acrolein (PE, PET)
CASRN: 107-02-8
STDS OSHA: 0.1 ppm, 0.25 mg/m³
TLV: 0.1 ppm, 0.25 mg/m³ TWA; 0.3 ppm, 0.8 mg/m³ STEL
DESC Volatile Liquid
HLTH: Irritation-Eyes, Nose, Throat, Lungs, Skin--Marked (14)
Mutagen (2).
IARC CARC: Animal Indefinite, '79.
SKIN ABS. Rabbit LD_{50}: 562 mg/kg
SKIN IRR: Yes
INGES ACUTE: Rabbit LD_{50}. 7 mg/kg
Rat LD_{50}. 46 mg/kg

Acrylic acid (PE)
CASRN: 79-10-7
STDS TLV: 10 ppm, 30 mg/m³ TWA
DESC: Semivolatile liquid
HLTH: Human Indefinite, '79.
SKIN ABS: Rabbit LD_{50}. 280 mg/kg
SKIN IRR. Severe
INGES ACUTE. Rat LD_{50}: 340 mg/kg

MONS 020558

Acrylonitrile (NIT, NOM, PU)
CASRN: 107-13-1
STDS. OSHA. 2 ppm
TLV: 2 ppm, 4.5 mg/m³ TWA
DESC. Volatile Liquid
HLTH: Suspect carcinogen (2) Reproductive Hazards (5).
CNS Oepression (7).
ACGIH: A1a (Human carcinogen)
IARC CARC: Human Suspect '79, '82.
IARC CARC: Animal Positive '79
IARC CARC: Animal Suspect '82.
SKIN ABS: Yes
SKIN IRR: Yes
INGES ACUTE. Rat LD_{50}: 82 mg/kg

Adiponitrile (N66)
CASRN: 111-69-3
DESC: Semivolatile Liquid
INGES ACUTE: Rat LD_{50}. 300 mg/kg

Allene (PU)
CASRN: 463-49-0
DESC: Gas

3-Aminobiphenyl (NOM)
CASRN: 2243-47-2

3-Amino-4-methylphenyl isocyanate (PU)

p-Aminophenol; 4-Aminophenol; 1-Amino-4-hydroxybenzene (KAP)
CASRN: 123-30-8
DESC: Solid, m.p. 188-190°C
SKIN IRR: Rabbit: 12.500 µg/24 H, mild
ORAL: Rat LD_{50}: 375 mg/kg

N-(3-Aminophenyl)benzamide (NOM)
CASRN: 16091-26-2

p-Aminophenyl phenyl ether; 4-Phenoxyaniline (KAP)
CASRN: 139-59-3
DESC: Solid, m.p. 82-84°C
SKIN IRR: Rabbit: 500 mg/24 H, mild
ORAL: Rat LD_{50}: 1100 mg/kg

Ammonia (NIT, NOM, PU)
CASRN: 7664-41-7
STDS: OSHA. 50 ppm, 35 mg/m³
TLV: 25 ppm, 18 mg/m³ TWA; 35 ppm, 27 mg/m³ STEL
DESC: Gas
HLTH: Acute lung damage/edema or other (11)
Irritation-Eyes, Nose, Throat, Bronchi, Lungs--Marked (14)
SKIN IRR: If concentrated
INGES ACUTE: Rat oral LD_{50}: 350 mg/kg

Aniline; Benzenamine (CRE, KAP, NOM)
CASRN. 62-53-3
STDS: OSHA: 5 ppm, 19 mg/m³
TLV· 2 ppm, 10 mg/m³ TWA; 5 ppm, 20 mg/m³ STEL
DESC: Semivolatile Liquid
HLTH. Methemoglobinia (13).
Suspect carcinogen (2).
Acute Toxicity--short-term high risk effects (4).
IARC CARC: Animal Indefinite '74.
IARC CARC: Human Negative '74.
SKIN ABS: Yes
INGES ACUTE: Rat LD_{50}: 440 mg/kg

Anthracene (CRE, CSPE, PE)
CASRN: 120-12-7
DESC: Solid, m.p. 216°C
SKIN IRR: Mild

Benzaldehyde (STY, SUL)
CASRN: 100-52-7
DESC· Semivolatile Liquid
SKIN IRR: Rabbit: 500 mg/24 H, moderate
ORAL: Rat LD_{50}: 1300 mg/kg

Benzanilide (NOM)
CASRN: 93-98-1
DESC. Solid, m.p. 162-164°C

Benz[a]anthracene; 1,2-Benzanthracene [a PAH] (CRE, PE, STY)
CASRN: 56-55-3
OESC. Solid, m.p. 157-159°C
IARC CARC: Animal Positive, '73.
IVN: Mouse LD_{Lo}: 10 mg/kg

Benzene (CSPE, EPO, NOM, PCP, PE, PET, PU, STY, SUL, XLPE)
CASRN· 71-43-2
STDS. OSHA: 10 ppm
TLV· 10 ppm, 30 mg/m³ TWA, 25 ppm, 75 mg/m³ STEL
DESC Volatile Liquid

MONS 020560

HLTH: Suspect Leukemogen (2).
Cumulative bone marrow damage (12)
ACGIH: A2 (Suspect carcinogen)
IARC CARC. Human Suspect '74 & '82
IARC CARC. Human Positive '82.
IARC CARC. Animal Suspect '82
IARC CARC. Animal '74.
Listed in NTP 2nd Annual Report on Carcinogens, '81.
SKIN ABS Slight
SKIN IRR: Mild
INGES ACUTE: Human TD_{Lo}: 130 mg/kg

Benzo[b]chrysene [a PAH] (CRE)
CASRN: 214-17-5
DESC: Solid
MUTAGEN
SKIN CARE. Mouse TD_{Lo}: 28 mg/kg

2,3-Benzofluoranthene, 3,4-Benzofluoranthene,
Benzo[b?]fluoranthene; Benz[e]acephenanthrylene [a PAH] (CRE, PE)
CASRN: 205-99-2
DESC: Solid, m.p 163-165°C
IARC CARC. Animal Positive, '73
TUMORIGEN: Mouse, skin: 88 ng/kg

Benzo[j]fluoranthene; 10,11-Benzofluoranthene [a PAH] (CRE, STY?)
CASRN: 205-82-3
DESC. Solid, m.p. 165°C
MUTAGEN
IARC CARC. Animal Positive, '73

Benzo[j,k]fluoranthene [a PAH] (STY?)
CASRN: Unavailable [Was benzo[j,k]fluorene misnamed?]

Benzo[k]fluoranthene, 11,12-Benzofluoranthene [a PAH] (CRE, STY?)
CASRN: 207-08-9
DESC Solid, m.p 217°C
MUTAGEN
CARC. Mouse skin: TD_{Lo}: 2820 mg/kg/47 W-intermittent

Benzofluorenes (CRE)

Benzo[a]fluorene: 1,2-Benzofluorene [a PAH] (PE, STY)
CASRN: 238-84-6

Benzo[b]fluorene, 2,3-Benzofluorene [a PAH] (PE, STY)
CASRN 243-17-4
DESC Solid, m p 209-210.5°C

Benzofuran (SUL)
CASRN (2,3-Isomer): 271-89-6
DESC: Semivolatile Liquid

Benzoic acid (NOM, PET, STY)
DESC Solid, m.p. 122°C, begins to sublime ~ 100°C
SKIN ABS Yes
SKIN IRR: Skin Human TD_{Lo}: 6 mg/kg
INGES ACUTE: Man LD_{50}: 500 mg/kg

Benzonitrile (CRE, KAP, NOM, PU)
CASRN: 100-47-0
DESC Semivolatile Liquid
SKIN IRR: Rabbit: 500 mg/24 H, moderate
ORAL: Rat LD_{Lo}: 720 mg/kg
IHL: Rat LC_{Lo}: 950 ppm/8 H
ORAL: Mouse LD_{50}: 1400 mg/kg

Benzo[g,h,i]perylene [a PAH] (STY)
CASRN: 191-24-2
MUTAGEN

Benzo[c]phenanthrene; 3,4-Benzphenanthrene [a PAH] (PE, STY)
CASRN: 195-19-7
DESC: Solid, m.p. 68°C
SKIN TUMORIGEN: Mouse TD_{Lo}: 940 mg/kg/39 W

Benzo[a]pyrene, B[a]P [a PAH] (CRE, PE)
CASRN: 50-32-8
DESC: Solid, m.p. 175-177°C
HLTH: IARC CARC: Animal Positive '73.
Listed in 2nd NTP Annual Report on Carcinogens, '81.
ACGIH: A2 (Suspect carcinogen)

Benzo[e]pyrene [a PAH] (CRE, PE, STY)
CASRN. 192-97-2
DESC: Solid, m.p. 180-182°C
IARC CARC: Animal Suspected, '73.

Benzo[b]thiophene; Thianaphthene (CRE)
CASRN: 95-15-8
DESC: Solid, m.p. 29-32°C

Biphenyl, Diphenyl (CRE, CSPE, EPO, NOM, PE, PET, STY, SUL)
CASRN 92-52-4
STDS OSHA 1 mg/m³
TLV: 0.2 ppm, 1.5 mg/m³ TWA, 0.6 ppm, 4 mg/m³ STEL
DESC. Solid, m.p. 69-72°C

HLTH: Irritation-Eye, Nose, Throat, Bronchi, Lungs, Skin--Moderate (15, Less than 3 mg/m³).
CNS Effects (7, Greater than 3 mg/m³)
INGES ACUTE: Rat LD_{50}. 3280 mg/kg

1,2-Butadiene; Methylallene (PE)
CASRN: 590-19-2
DESC Gas

1,3-Butadiene (CSPE, NIT, PE, PU)
CASRN: 106-99-0
STDS OSHA 1000 ppm, 2200 mg/m³
TLV: 1000 ppm, 2200 mg/m³ TWA, 1250 ppm, 2750 mg/m³ STEL
DESC. Gas
HLTH. Irritation-Eyes, Nose, Throat--Mild (16, Less than 3000 ppm)
INGES ACUTE: Rat LD_{50}. 5480 mg/kg
TERATOGEN (Reference 7)
NTP AND OSHA CARC: Animal carcinogen by inhalation (References 7-9)

n-Butanol (PU)
CASRN: 71-36-3
STDS: OSHA: 100 ppm, 300 mg/m³
TLV: C 50 ppm, C 150 mg/m³ TWA
OESC. Volatile Liquid
HLTH. Irritation-Eyes, Nose, Throat--Moderate (15).
Hearing loss (7).
Narcosis (8).
SKIN ABS: Yes
SKIN IRR: Severe
INGES ACUTE: Rat LD_{50}: 790 mg/kg

1-Butene; α-Butylene (CSPE; EPO)
CASRN: 106-98-9
DESC. Gas

2-Butenenitrile; Crotonitrile (NOM)
CASRN (mixt. of trans- and cis-): 4786-20-3
DESC: Volatile Liquid

3-Butenenitrile; 1-Butene-4-nitrile, Allyl cyanide (NOM)
CASRN: 109-75-1
OESC: Volatile Liquid
SKIN IRR: 10 mg/24 H open, mild
ORAL Rat LD_{50}: 115 mg/kg
SKIN: Rabbit LD_{50}: 1410 mg/kg

Butyraldehyde; Butanal (PE)
CASRN: 123-72-8
DESC: Volatile Liquid
IHL: Human TC_{Lo}: 580 mg/m³
ORAL Rat LD_{50}: 2490 mg/kg
SKIN IRR: Rabbit: 500 mg/24 H, severe

Butyric acid; Butanoic acid (PE)
CASRN: 107-92-6
DESC: Semivolatile Liquid
MUTAGEN
SKIN IRR: Rabbit: 10 mg/24 H, severe
EYE IRR: Rabbit: 0.25 mg, severe
ORAL: Rat LD_{50}: 2940 mg/kg

Butyrolactone (PE)
β-Butyrolactone; 4-Methyl-2-oxetenone
CASRN: 3068-88-0
SKIN IRR: Rabbit: 500 mg, open
ORAL: Rat LD_{50}: 17 g/kg
IARC CARC: Animal positive, '76
γ-Butyrolactone
CASRN: 96-48-0
DESC: Semivolatile Liquid
IARC CARC: Negative, '76
TUMORIGEN: Mouse, skin: 50 g/kg
IPR: Mouse LD_{50}: 1100 mg/kg

Caproic acid; Hexanoic acid (PE)
CASRN: 142-62-1
DESC: Semivolatile Liquid
SKIN IRR: Rabbit: 10 mg/24 H, mild
ORAL: Rat LD_{50}: 3000 mg/kg
SKIN: Rabbit LD_{50}: 630 mg/kg

Caprolactam dust (NY6, N66, 610)
CASRN: 105-60-2
STOS. TLV: 1 mg/m³ TWA; 3 mg/m³ STEL
DESC: Solid, m.p. 70-72°C
HLTH: Irritation-Eyes, Nose, Throat, Skin--Moderate (15, Less than 2 mg/m³)
CNS Effects (7, Greater than 2 mg/m³)
SKIN ABS: LD_{Lo}: 1410 mg/kg
SKIN IRR: Mild
INGES ACUTE: Rat LD_{50}: 2140 mg/kg

Caprolactam (NY6, N66, 610)
CASRN: 105-60-2
STOS TLV. 5 ppm, 20 mg/m³ TWA; 10 ppm, 40 mg/m³ STEL
DESC. Solid, m p. 70-72°C
HLTH: Irritation-Eyes, Nose, Throat, Skin--Moderate (15, Less than 10 ppm)
CNS Effects (7, Greater than 10 ppm).
Vapor less irritating than dust to respiratory tract
See Caprolactam dust above for toxic, oral, and skin information

MONS 020564

Carbazole (CRE)
CASRN. 86-74-8
DESC: Solid, m.p 245-246°C
ORAL: Rat LD_{Lo}: 500 mg/kg
IPR: Mouse LD_{50}: 200 mg/kg

Carbon dioxide (CSPE, EPO, FEP, KAP, NOM, PAP, PE, PET, PU, SUL, TEF, VIT)
CASRN 124-38-9
STDS OSHA: 5000 ppm, 9000 mg/m³
TLV: 5000 ppm, 9000 mg/m³ TWA, 15,000 ppm, 27,000 mg/m³ STEL
DESC. Gas
HLTH: Simple Asphyxiant (17, Less than 10,000 ppm).
SKIN. Direct contact with dry ice can cause freezing of tissue

Carbon monoxide (CSPE, EPO, FEP, HAL, KAP, NEO, NOM, NY6, PAP, PE, PET, PU, SUL, TFE, TFZ, VIT)
CASRN. 630-08-0
STDS: OSHA: 50 ppm, 55 mg/m³
TLV. 50 ppm, 55 mg/m³ TWA; 400 ppm, 440 mg/m³ STEL
DESC: Gas
HLTH: Asphyxiation, Chemical anoxia (17, Less than 75 ppm)

Carbon tetrafluoride (TEF, FEP)
CASRN: 75-73-0
DESC: Gas
IHL: Rat LC_{Lo}: 895,000 ppm/15 min

Carbonyl fluoride (HAL, TFZ)
CASRN: 353-50-4
STDS: TLV: 2 ppm, 5 mg/m³ TWA, 5 ppm, 15 mg/m³ STEL
DESC: Gas

Chloroform; Trichloromethane (XLPE)
CASRN. 67-66-3
STDS. OSHA: C 50 ppm, C 240 mg/m³
TLV: 10 ppm, 50 mg/m³ TWA; 50 ppm, 225 mg/m³ STEL
DESC: Volatile Liquid
HLTH Suspect Carcinogen (2). Cumulative liver and kidney damage (3)
Narcosis (8).
ACGIH: A2 (Suspect carcinogen)
IARC CARC: Animal Suspect, '72
IARC CARC: Animal Positive, '78
IARC CARC. Human Suspect, '81.
Listed in 2nd NTP Annual Report on Carcinogens, '81

Chrysene [a PAH] (CRE, PE, STY)
CASRN. 218-01-9
STDS TLV Suspect carcinogen
DESC Solid, m.p 254-255°C
IARC CARC Animal Positive '73
SKIN ABS Skin carcinogen Mouse 3 6 mg/kg

Cinnamyl alcohol (STY)
CASRN: 104-54-1
DESC. Solid, m.p. 33-35°C
TUMORIGEN: Mouse, ipr: 1400 mg/kg
ORAL. Rat LD_{50}: 2000 mg/kg
SKIN IRR: Rabbit. 522 mg/24 H, moderate

Cresol (CRE, EPO, SUL)
CASRN: 1319-77-3
STDS: OSHA: 5 ppm, 22 mg/m³
TLV: 5 ppm, 22 mg/m³ TWA
DESC. Solid or Semivolatile Liquid (depending on isomer)
HLTH: Irritation-Eyes, Skin--Marked (14).
Acute Toxicity-(CNS) (4).
Cumulative liver, cardiovascular, kidney damage (3).
SKIN ABS. Yes
SKIN IRR: Yes
INGES ACUTE: Varies with isomer:
Rat LD_{50}: approximately 200 mg/kg
o-Cresol is the most toxic orally

Crotonic acid; trans-2-Butenoic acid (PE)
CASRN 3724-65-0
DESC: Solid, m.p. 72-74°C
ORAL. Rat LD_{50}. 1000 mg/kg
SKIN: Guinea pig LD_{50}: 600 mg/kg
SKIN IRR: Rabbit: 10 mg/24 H

Cumene; Isopropylbenzene (STY, XLPE)
CASRN: 98-82-8
STDS. OSHA: 50 ppm, 245 mg/m³
TLV: 50 ppm, 245 mg/m³ TWA; 75 ppm, 365 mg/m³ STEL
DESC: Semivolatile Liquid
HLTH: Narcosis (8).
Irritation-Eyes, Skin--Moderate (15, Less than 100 ppm).
SKIN ABS Yes
SKIN IRR: Yes, Primary Irritant
INGES ACUTE: Rat LD_{50}: 1400 mg/kg

Cyanoanilines; Aminobenzonitriles (NOM)

m-Cyanoaniline
CASRN: 2237-30-1
DESC. Solid, m.p. 51-53°C
o-Cyanoaniline; Anthranilonitrile
CASRN: 1885-29-6
DESC Solid, m.p. 47-49°C
IPR Mouse LD_{50} 180 mg/kg
p-Cyanoaniline
CASRN 873-74-5
DESC Solid, m.p. 83-85°C
IPR Mouse LD_{50}. 155 mg/kg

3-Cyanobenzoic acid (EPO)
CASRN: 1877-72-1
DESC: Solid, m.p. 222-224°

3-Cyanobiphenyl (NOM)

Cyanogen (NOM)
CASRN: 460-19-5
STDS TLV: 10 ppm TWA
DESC. Gas
HLTH: Irritation-Eyes, Nose, Throat--Moderate (15).
Acute Toxicity (Cyanosis) (4).

N-(3-Cyanophenyl)benzamide (NOM)

Cyclopentadiene (EPO)
CASRN: 542-92-7
DESC. Volatile Liquid
HLTH. Irritation-Eyes, Nose, Throat--Moderate (15, Less than 150 ppm).

Cyclopentanone (N66)
CASRN. 120-92-3
DESC: Semivolatile Liquid
SKIN IRR: Rabbit: 500 mg/24 H
IPR: Mouse LD_{50}: 1950 mg/kg
SCU: Mouse LD_{Lo}: 2600 mg/kg

Cyclopropane (PE)
CASRN: 75-19-4
DESC: Gas

Decachlorobiphenyl (PCP)
CASRN: 2051-24-3
DESC: Solid, m p 305-306°C

Decafluorobutane (FEP, TEF)
CASRN: 355-25-9

Dibanz[a,h]anthracene; 1,2,5,6-Dibenzanthracene [a PAH] (CRE)
CASRN: 53-70-3
DESC: Solid, m.p. 266-267°C
MUTAGEN
IARC CARC: Animal Positive, '73.
IVN: Mouse LD_{Lo}: 10 mg/kg

Dibenzofuran (CRE, KAP, SUL)
CASRN: 132-64-9
DESC. Solid, m p. 83-84°C

1,3-Dicyanobenzene; Isophthalonitrile (NOM)
CASRN. 626-17-5
STDS. TLV-TWA 5 mg/m³
DESC: Solid, m p. 160-162°C
ORAL. Rat LD_{50}. 1860 mg/kg
ORAL. Mouse LD_{50}: 178 mg/kg

1,4-Dicyanobenzene; Terephthalonitrile, p-Dicyanobenzene (KAP, PU)
CASRN: 623-26-7
DESC. Solid, m.p. 224-227°C
EYE IRR: Rabbit: 500 mg/24 H, moderate
ORAL: Rat LD_{50}: 21 g/kg

Dihydroanthracene (PE)
CASRN (9,10-isomer): 613-31-0
DESC: Solid, m.p. 108-110°C

Diisobutyl phthelate (NEO)
CASRN: 84-69-5
DESC: Semivolatile Liquid
ORAL: Rat LD_{50}: 20 g/kg
ORAL Mouse [illegible] 10 g/kg
SKIN: Guinea pig LD_{50}: 10 g/kg

Dimethyl ether; Methyl ether (PU)
CASRN: 115-10-6
DESC: Gas
INHL: Mouse LC_{50}: 386 ppm/15 min

Dimethylnaphthalene (CRE, CSPE, SUL)
CASRN: 28804-88-8
DESC: Semivolatile Liquids or Solids
1,6-Dimethylnaonthalene
CASRN: 575-43-9
DESC: Semivolatile Liquid
ORAL: Rat LD_{LO}: 5000 mg/kg

Dioctyl phthalate (NEO)
DESC: Semivolatile Liquid
SKIN IRR: Mild
INGES ACUTE: Mouse LD_{50}: 6513 mg/kg [Di-n-octyl phthalate, CASRN 117-84-0]
Rat LD_{50}. 31 g/kg [Bis(2-ethylhexyl) phthalate, CASRN 117-81-7]

1,4-Dioxane, Diethylene Dioxide (NOM)
CASRN 123-91-1
STDS. OSHA: 100 ppm, 360 mg/m³
TLV: 25 ppm, 90 mg/m³ TWA; 100 ppm, 360 mg/m³ STEL
DESC Volatile Liquid

MONS 020568

HLTH: Suspect carcinogen (2). Cumulative liver and kidney damage (3)
Irritation-Eyes, Nose, Throat--Mild (16).
IARC CARC. Animal Positive, '76.
Listed in 2nd NTP Annuel Report on Carciongens, '81
SKIN ABS. Yes
SKIN IRR: Mild
INGES ACUTE: Rat LD_{50}: 4200 mg/kg

Diphenylethene (STY)
CASRN (1,2-isomer): 103-29-7
DESC. Solid, m.p. 50-53°C

Diphenyl ether (EPO, SUL)
CASRN 101-84-8
STDS. OSHA: 1 ppm, 7 mg/m³
TLV: 1 ppm, 7 mg/m³ TWA; 2 ppm, 14 mg/m³ STEL
DESC. Volatile Liquid
HLTH: Nausea (7).
Irritation-Eyes, Skin--Mild (16)
Cumulative liver and kidney damage (3).
SKIN IRR: Mild
INGES ACUTE: Rat LD_{50}: 3370 mg/kg

Dipropylene glycol methyl ether (XLPE)
CASRN: 34590-94-8
STDS: OSHA: 100 ppm, 600 mg/m³
TLV: 100 ppm, 600 mg/m³ TWA, 150 ppm, 900 mg/m³ STEL
DESC: Semivolatile Liquid
HLTH: Irritation-Eyes, Nose--Moderate (15). Slight Narcosis (8)
SKIN ABS: Yes
SKIN IRR: Mild
INGES ACUTE: Rat LD_{50}: 4900 mg/kg

Divinyl terephthalate (PET)
CASRN. 94-49-5

Ethane (CSPE, EPO, NOM, PE, PET, PU, SUL)
CASRN. 74-84-0
DESC: Gas
HLTH: Explosive (18).
Simple Asphyxiation (17, If oxygen level is 18% by volume)

2-Ethoxyethanol (PU)
CASRN. 110-80-5
STDS: OSHA. 200 ppm, 740 mg/m³
TLV: 50 ppm, 185 mg/m³ TWA, 100 ppm, 370 mg/m³ STEL
(NOTE: Probable change to 5 ppm, with no STEL. Skin notation will be continued.)
DESC Semivolatile Liquid
HLTH Irritation-Eyes, Nose--Moderate (15)
Cumulative blood disturbances (12)

SKIN ABS: Yes
SKIN IRR: Mild
INGES ACUTE: Rat LD_{50}: 3000 mg/kg

Ethyl alcohol, Ethanol (PE, PU)
CASRN: 64-17-5
STDS: OSHA: 1000 ppm, 1900 mg/m³
TLV 1000 ppm, 1900 mg/m³ TWA
DESC: Volatile Liquid
HLTH: Irritation-Eyes, Nose, Throat--Marked (14, Less than 3000 ppm)
Narcosis (8).
Reproductive impairment (5, Greater than 3000 ppm)
SKIN ABS: Rabbit LD_{Lo}: 20 g/kg
SKIN IRR: Severe
INGES ACUTE: LD_{50}: 7060 mg/kg

Ethylbenzene (EPO, NIT, PE, PET, STY, SUL)
CASRN: 100-41-4
STDS: OSHA: 100 ppm, 435 mg/m³
TLV: 100 ppm, 435 mg/m³ TWA, 125 ppm, 545 mg/m³ STEL
DESC: Semivolatile Liquid
HLTH: Irritation-Eyes, Nose, Throat, Skin--Moderate (15, Less than 200 ppm)
Narcosis (8).
SKIN ABS: Rabbit LD_{50} 3500 mg/kg
SKIN IRR: Mild
INGES ACUTE: Rat LD_{50}: 3500 mg/kg

Ethyl chloride; Chloroethane (EPO)
CASRN: 75-00-3
STDS: OSHA: 1000 ppm, 2600 mg/m³
TLV: 1000 ppm, 2600 mg/m³ TWA; 1250 ppm, 3250 mg/m³ STEL
DESC: Gas
HLTH: Narcosis (8, Greater than 5000 ppm).
SKIN IRR: Frostbite possible if liquefied gas is spilled on skin.

Ethylene; Ethene (EPO, NOM, PAP, PE, PET, PU, SUL, TFZ)
CASRN: 74-85-1
DESC: Gas
HLTH: Simple Asphyxiation (17, If oxygen level is 18% by volume).
Explosive (18).
ACGIH: E (Simple asphyxiants)

Ethylene dibenzoate (PET)
CASRN: 94-49-5

Ethylene glycol, particulate (PET)
CASRN 107-21-1
STDS: OSHA: 1 0 mg/m³
TLV 10 mg/m³ TWA
DESC Volatile Liquid
HLTH Irritation-Eyes, Nose, Throat--Moderate (15) CNS depression (7)

SKIN ABS. Rabbit LD_{50}: 19,530 mg/kg
SKIN IRR: Mild
INGES ACUTE: Human LD_{Lo}: 710 mg/kg

Ethylene glycol, vapor (PET)
CASRN: 107-21-1
STDS TLV. C 50 ppm, C 125 mg/m³ TWA
DESC. Vapor
HLTH: Irritation-Eyes, Nose, Throat--Moderate (15). CNS depression (7)
SKIN ABS: Rabbit LD_{50}. 19,530 mg/kg
SKIN IRR: Mild
INGES ACUTE. Human LD_{Lo}: 710 mg/kg

Ethylmethylphenol; ethylcresol (CRE)
CASRN: 1687-61-2
DESC. Solid?
6-Ethyl-m-cresol
UNKNOWN ROUTE: Rat LD_{50}: 530 mg/kg

Ethylphenol (SUL)
2-Ethylphenol
CASRN: 90-00-6
DESC: Semivolatile Liquid
CARC: Mouse Skin TD_{Lo}. 3100 mg/kg/12 W, intermittent
3-Ethylphenol
CASRN: 620-17-7
DESC: Semivolatile Liquid
4-Ethylphenol
CASRN: 123-07-9
DESC: Solid, m.p. 42-45°C

Fluoranthene [a PAH] (CRE, PE, STY)
CASRN: 206-44-0
DESC. Solid, m.p. 107-110°C
SKIN TUMORIGEN: Mouse TD_{Lo}: 280 mg/kg/58 W
ORAL: Rat LD_{50}: 2000 mg/kg

Fluorene [a PAH] (CRE, CSPE, PE, STY)
CASRN: 86-73-7
DESC: Solid, m.p. 112-115°C

Formaldehyde; Methanal (PE, PET, STY)
CASRN: 50-00-0
STDS: DSHA: 3 ppm
TLV: 2 ppm, 3 mg/m³ TWA
DESC Gas
HLTH. Irritation-Eyes, Lungs, Skin--Marked (14).
Suspect Carcinogen/Mutagen (2).
IARC CARC: Animal Positive, '82.
IARC CARC: Human indefinite, '82.
ACGIH: A2 (Suspect carcinogen)
Listed in 2nd NTP Annual Report on Carcinogens, '81

Thiobutyric acid, S-decyl ester (XLPE)

Toluene; Methylbenzene (CSPE, EPO, NIT, NOM, PE, PET, PU, STY, SUL, XLPE)
CASRN: 108-88-3
STDS: OSHA: 200 ppm
TLV: 100 ppm, 375 mg/m³ TWA; 150 ppm, 560 mg/m³ STEL
DESC. Volatile Liquid
HLTH: Irritation-Eyes, Nose, Throat--Moderate (15).
Narcosis (8).
Suspect teratogen (5).
Mutegen (2).
SKIN ABS: Yes
SKIN IRR: Mild
INGES ACUTE: Rat LD_{50}: 5000 mg/kg

2,4-Toluenediamine; 2,4-Diaminotoluene (PU)
CASRN: 95-80-7
DESC: Solid, m.p. 97-99°C
HLTH: IARC CARC: Animal Positive, '78 and '82.
Listed in 2nd NTP Annual Report on Carcinogens, '81.
SKIN IRR: Mild
INGES ACUTE: Rat LD_{50}: 260 mg/kg

Toluene 2,4-diisocyanate; TDI; Tolylene 2,4-diisocyanate (PU)
CASRN: 584-84-9
STDS: OSHA: C 0.02 mg/m³
TLV: C 0.02 ppm, C 0.14 mg/m³ TWA
DESC: Semivolatile Liquid
HLTH: Asthma (9).
Irritation-Eyes, Nose, Throat, Bronchi, Lungs--Marked (14).
Dermatitis (3).
SKIN IRR: Severe
INGES ACUTE: LD_{50}: 5800 mg/kg

Toluene 2,6-diisocyanate (PU)
CASRN: 91-08-7
DESC: Semivolatile Liquid
HLTH: Respiratory sensitization (Asthma) (9).

m-Toluidine (CRE)
CASRN: 108-44-1
DESC: Semivolatile liquid
SKIN IRR: Rabbit: 500 mg/24 H, severe
EYE IRR: Rabbit: 20 mg/24 H, severe
ORAL: Rat LD_{50}: 450 mg/kg

o-Toluidine (CRE)
CASRN: 95-53-4
STDS: OSHA: 5 ppm, 22 mg/m³
TLV: 2 ppm, 9 mg/m³
DESC Semivolatile Liquid

MONS 020587

n-Hexadecane (NEO)
CASRN: 544-76-3
DESC: Semivolatile Liquid (freezes at 18 2°C)

Hexafluoropropane (FEP, TEF)
CASRN: 27070-61-7; (1,1,1,3,3,3-) 690-39-1, (1,1,2,2,3,3-) 680-00-2, (1,1,1,2,2,3-) 677-56-5, (1,1,1,2,3,3-) 431-63-0
DESC: Gas

Hexafluoropropylene; Hexafluoropropene (TEF, FEP, VIT)
CASRN: 116-15-4
DESC: Gas
IHL Rat LC_{Lo}: 20,000 mg/m³/2 H

Hexanal; Hexaldehyde, Caproaldehyde (PE)
CASRN: 66-25-1
DESC: Semivolatile Liquid
ORAL: Rat LD_{50}: 4890 mg/kg
IHL: Rat LC_{Lo}: 2000 ppm/4 H
SKIN IRR: Rabbit: 10 mg/24 H, mild

n-Hexane (PE)
CASRN: 110-54-3
STDS: OSHA: 500 ppm, 1800 mg/m³/15 min
TLV: 50 ppm, 180 mg/m³ TLV
DESC: Volatile Liquid
HLTH: Nervous system disturbances--polyneuropathy (7)
Nervous system disturbances--narcosis (8).
SKIN IRR: Mild
IHL: Human TC_{Lo}: 5000 ppm/10 min

1-Hexene (CSPE, PE)
CASRN: 592-41-6
DESC: Volatile Liquid

Hydrogen (EPO, KAP, NIT, NOM, PAP, PE)
CASRN: 1333-74-0
DESC: Gas
HLTH: Simple Asphyxiation (17, If oxygen level is 18% by volume)
Explosive (18).

Hydrogen chloride (gas, anhydrous) (CSPE, HAL, NEO)
CASRN: 7467-01-0
STDS OSHA: C 5 ppm, C 7 mg/m³
TLV: C 5 ppm, C 7 mg/m³ TWA
DESC: Gas
HLTH: Irritation- Eyes, Nose, Throat--Marked (14)
Lung edema (11)
Dental erosion (3)

Hydrogen cyanide (gas) (KAP, N66, NEO, NIT, NOM, PU)
CASRN: 74-90-8
STDS: OSHA: 10 ppm, 11 mg/m³
TLV: C 10 ppm, C 10 mg/m³ TWA
DESC Gas
HLTH. Acute systemic toxicity (4).
Cumulative systemic toxicity (Cyanosis) (3).

Hydrogen fluoride (gas, anhydrous) (HAL, TFZ, VIT)
CASRN: 7664-39-3
STDS: OSHA: 3 ppm
TLV: 3 ppm, 2.5 mg/m³ TWA; 6 ppm, 5 mg/m³ STEL
DESC· Gas
HLTH. Irritation-Eyes, Nose, Throat, Skin--Marked (14).
Acute lung damage (11).
Cumulative bone damage (3)

Hydrogen sulfide (NEO)
CASRN: 7783-06-4
STDS: OSHA: 20 ppm
TLV. 10 ppm, 14 mg/m³ TWA; 15 ppm, 21 mg/m³ STEL
DESC. Gas
HLTH: Acute systemic toxicity (4).
Irritation-Eyes (Conjunctivitis), Lungs--Moderate (15).
CNS effects (7).

Hydroxyethyl terephthalate monoester (PET)

2-Hydroxyphenyl-2-phenylpropane (SUL)

Hydroxyvaleric acid (PE)
CASRN: 30853-48-0
DESC. (2-isomer) Solid, m.p. 34°C (sublimes)

Indan (EPO, PE)
CASRN. 496-11-7
DESC: Semivolatile Liquid
ORAL: Rat LD_{Lo}: 5000 mg/kg

Indene (CSPE, EPO, PE, PU, STY, SUL)
CASRN: 95-13-6
STDS: TLV. 10 ppm, 45 mg/m³ TWA; 15 ppm, 70 mg/m³ STEL
DESC. Semivolatile Liquid
HLTH. Irritation-Eyes, Nose, Throat--Moderate (15).
Cumulative liver and kidney damage (3).

Indole (CRE)
CASRN. 120-72-9
DESC. Solid, m.p. 52-54°C
ORAL. Rat LD_{50}: 1000 mg/kg
SKIN: Rabbit LD_{50}: 790 mg/kg

Isobutyraldehyde (PE)
CASRN. 78-84-2
DESC. Volatile Liquid
IHL: Rat LC_{LO}: 8000 ppm/4 H
ORAL: Rat LD_{50}: 2810 mg/kg
SKIN IRR: Rabbit: 500 mg/24 H, severe

Isoprene (CSPE)
CASRN: 78-79-5
DESC. Volatile Liquid (b.p. 34°C)

Isovaleric acid (PE)
CASRN: 503-74-2
DESC Semivolatile Liquid
ORAL: Rat LD_{50}: 2000 mg/kg
SKIN: Rabbit LD_{50}: 310 mg/kg
SKIN IRR: Rabbit: 500 mg/24 H, moderate

Methacrylonitrile (NIT, PU)
CASRN: 126-98-7
TLV: 1 ppm, 3 mg/m³ TWA; skin warning
DESC: Volatile Liquid
SKIN IRR: Rabbit: 200 mg, mild
ORAL: Rat LD_{50}: 250 mg/kg

Methane (CSPE, EPO, KAP, NEO, NIT, NOM, PAP, PE, PET, PU, SUL)
CASRN: 74-82-8
DESC: Gas
HLTH: Explosive (18).
Asphyxiant (17, If oxygen level is 18% by volume).
ACGIH: E (Simple asphyxiant)

Methyl alcohol; Methanol (NOM, PU)
CASRN: 67-56-1
STDS: OSHA: 200 ppm, 260 mg/m³
TLV: 200 ppm, 260 mg/m³ TWA; 250 ppm, 310 mg/m³ STEL
DESC: Volatile Liquid
HLTH: Cumulative CNS effects (7, Greater than 400 ppm).
Narcosis (8).
Irritation-Eyes, Nose, Throat--Mild (16, Less than 400 ppm)

Methylanthracenes [PAHs] (PE)
CASRN (2-) 613-12-7; (9-) 779-02-2
DESC (2-) Semivolatile Liquid, (9-) solid, m.p. 71-79°C

Methylbenzofuran (SUL)
CASRN: 25586-38-3
DESC. (2-,3-,5-, or 7-isomer) Semivolatile liquid

4-Methylbiphenyl; 4-Phenyltoluene (STY)
CASRN. 644-08-6
DESC: Solid, m.p. 44-47°C
ORAL: Rat LD_{50}: 2570 mg/kg

1-Methylbutyl isobutyrate; Propanoic acid, 2-methyl-, 1-methylbutyl ester (MEO)
CASRN: 54340-93-1

Methyl chloride; Chloromethane (EPO)
CASRN: 74-87-3
STDS: OSHA: 100 ppm
TLV: 50 ppm, 105 mg/m³ TWA; 100 ppm 205 mg/m³ STEL
DESC: Gas
HLTH: Acute CNS effects (4).
Chronic CNS effects (7).
Cumulative liver and kidney damage (3)
SKIN ABS. Yes

3-Methylcholanthrene [a PAH] (STY)
CASRN: 56-49-5
DESC: Solid, m.p. 178-180°C
TUMORIGEN: Oral: Rat TD_{Lo}: 200 mg/kg
TUMORIGEN: Skin: Rat TD_{Lo}: 700 mg/kg/25 W-intermittent
TERATOGEN

2-Methyl-1,3-dioxolane (PET)
CASRN: 497-26-7
DESC: Volatile Liquid

4,5-Methylenephenanthrene (PE)
CASRN: 203-64-5
DESC: Semivolatile Liquid

Methylethylbenzenes; Ethyltoluenes (SUL)
2-Ethyltoluene
CASRN: 611-14-3
DESC. Semivolatile Liquid
ORAL Rat LD_{Lo}: 5000 mg/kg
3-Ethyltoluene
CASRN. 620-14-4
DESC: Semivolatile Liquid
4-Ethyltoluene
CASRN. 622-96-8
DESC. Semivolatile Liquid
ORAL: Rat LD_{Lo} 5000 mg/kg

MONS 020576

Methyl ethyl ketone, 2-Butanone; MEK (PE)
CASRN: 78-93-3
STDS: OSHA: 200 ppm, 590 mg/m³
TLV: 200 ppm, 590 mg/m³ TWA: 300 ppm, 885 mg/m³ STEL
DESC: Volatile Liquid
HLTH: Irritation-Eyes, Nose, Throat--Moderate (15). Narcosis (3).
SKIN IRR: Moderate
INGES ACUTE Rat LD_{50}: 2737 mg/kg

Methylfluorenes [PAHs] (CRE, PE)
CASRN: (1-) 1730-37-6; (9-) 2523-37-7
DESC (1-) Solid, m.p 84-86°C; (9-) Semivolatile Liquid

Methylindene (STY, SUL)
CASRN: 29036-25-7
DESC: Semivolatile liquid

Methyl-4,5-methylenephenanthrene; Methyl-4H-cyclopenta[def]phenanthrene (PE)
CASRN: 58548-39-3

1-Methylnaphthalene (CRE, CSPE, PE, STY, SUL)
CASRN: 1321-94-4
DESC: Semivolatile Liquid
INGES ACUTE: Rat LD_{50}: 4360 mg/kg

2-Methylnaphthalene (CRE, CSPE, PE, STY)
CASRN: 91-57-6
DESC: Solid, m.p. 34-36°C
ORAL: Rat LD_{Lo}: 5000 mg/kg

Methylphenanthrene (PE)
1-Methyl isomer
CASRN: 832-69-9
MUTAGEN
2-Methyl isomer
CASRN: 2531-84-2
DESC: Solid, m.p. 57-59°C
MUTAGEN

2-Methylpyridine; α-Picoline (PU)
CASRN: 109-06-8
DESC: Semivolatile Liquid
SKIN IRR: Rabbit: 10 mg/24 H, mild
EYE IRR: Rabbit. 0 750 mg, severe
ORAL Rat LD_{50}: 790 mg/kg
IHL Rat LC_{Lo} 4000 ppm/4 H
SKIN: Rabbit LD_{50} 410 mg/kg

MONS 020577

4-Methylpyridine; γ-Picoline (PU)
CASRN: 108-89-4
DESC: Semivolatile Liquid
SKIN IRR: Rabbit: 10 mg/24 H, severe
EYE IRR Rabbit: 0.750 mg, severe
ORAL. Rat LD_{50}: 1290 mg/kg
IHL: Rat LC_{Lo}. 1000 ppm/4 H
SKIN: Rabbit LD_{50}: 270 mg/kg

α-Methylstyrene; 2-Phenyl-1-propene (STY, XLPE)
CASRN 98-83-9
STDS: OSHA: C 100 ppm, C 480 mg/m³
TLV: 50 ppm, 240 mg/m³ TWA; 100 ppm, 485 mg/m³ STEL
DESC. Semivolatile Liquid
HLTH. Irritation-Eyes, Nose, Throat--Mild (15).
CNS effects (7).
Narcosis (8).
SKIN IRR: Moderate

2-(Methylthio)benzothiazole (NEO)
CASRN. 615-22-5
DESC Solid, m.p. 52°C

Methyl vinyl ketone (PE)
CASRN: 78-94-4
DESC. Volatile Liquid
IPR: Mouse LD_{50}: 80 mg/kg

Naphthalene (CRE, CSPE, EPO, PE, PET, STY, SUL)
CASRN: 91-20-3
STDS: OSHA: 10 ppm, 50 mg/m³
TLV: 10 ppm, 50 mg/m³ TWA; 15 ppm, 75 mg/m³ STEL
DESC. Solid, m.p. 80°C, sublimes at room temperature
HLTH: Irritation-Eyes, Nose, Throat--Marked (14).
Ocular damage/Anemia/CNS damage (3)
Suspect carcinogen (2).
SKIN IRR: Mild
INGES ACUTE. Human LD_{Lo}. 74 to 100 mg/kg

α-Naphthol; 1-Naphthol (CRE)
CASRN: 90-15-3
DESC: Solid, m.p. 95-96°C
SKIN IRR. 500 mg/24 H, severe
EYE IRR: Rabbit, 1 mg, severe
MUTAGEN
ORAL Rat LD_{50}. 2,400 mg/kg
SKIN Rabbit LD_{50} 880 mg/kg

MONS 020578

β-Naphthol; 2-Naphthol (CRE)
CASRN: 135-19-3
DESC: Solid, m.p. 122-123°C
SKIN IRR: Mild
INGES ACUTE: Rat LD_{50}: 2420 mg/kg

α-Naphthylamine; 1-Aminonaphthalene (CRE)
CASRN 134-32-7
STDS: OSHA: 29 CFR 1910.1004
DESC. Solid, m.p. 48-50°C
HLTH: Cancer-Bladder (suspect) (1).
IARC CARC: Animal Indefinite, '74
IARC CARC: Human Suspect, '74.
SKIN ABS: Yes
INGES ACUTE. Rat LD_{50}: 779 mg/kg

β-Naphthylamine, 2-Aminonaphthalene (CRE)
CASRN: 91-59-8
STDS. OSHA: 29 CFR 1910.1009
DESC. Solid, m.p. 111-113°C
HLTH: Cancer-Bladder (1).
ACGIH: A2 (Human Carcinogen)
IARC CARC: Animal Positive, '74.
IARC CARC: Human Positive, '74
INGES ACUTE: Rat LD_{50}: 727 mg/kg

Nitric oxide (NOM)
CASRN: 10102-43-9
STDS: OSHA: 25 ppm, 30 mg/m³
TLV: 25 ppm, 30 mg/m³ TWA: 35 ppm, 45 mg/m³ STEL
DESC Gas
HLTH: Methemoglobinemia (13, Less than 50 ppm).
CNS effects (7, Greater than 50 ppm). Dalayed lung damage (10)

Nitromethane (NOM)
CASRN 75-52-5
STDS. OSHA: 100 ppm, 250 mg/m³
TLV: 100 ppm, 250 mg/m³ TWA; 150 ppm, 375 mg/m³ STEL
DESC. Volatile Liquid
HLTH. Irritation-Eyes, Nose, Throat, Skin--Mild (16, Less than 300 ppm)
Narcosis (8, Greater than 300 ppm).
Cumulative liver and lung damage (3).
INGES ACUTE: Rabbit LD_{Lo}: 750 mg/kg

Nitrous oxide (NLM, PU)
CASRN. 10024-97-2
DESC. Gas
HLTH: Reproductive Hazard (Male and Female) (5, Greater than 100 ppm)
CNS effects (7)

n-Nonacosane (NEO)
CASRN: 630-03-5
DESC: Solid, m.p. 66-67°C

Nonylphenol (NEO)
CASRN: 25154-52-3
DESC: Semivolatile Liquid
SKIN IRR: Rabbit: 10 mg/24 hr, severe
EYE IRR. Rabbit: 0.050 mg, severe

Octachlorodibenzo-p-dioxin (PCP)
CASRN: 3268-87-9
DESC: Solid
EYE IRR: Rabbit: 2 mg, mild
SKIN TUMORIGEN: Mouse TD_{Lo}: 290 mg/kg/60 W
IARC CARC: Animal Indefinite, '77.

Octachlorodibenzofuran (PCP)
CASRN. 39001-02-0

Octachloronaphthalene; Perchloronaphtnalene (PCP)
CASRN: 2234-13-1
STOS: OSHA: 0.1 mg/m³
TLV: 0.1 mg/m³ TWA; 0.3 mg/m³ STEL
DESC: Solid, m.p. 197-198°C
HLTH: Cumulative liver damage/Chloracne (3).
SKIN ABS: Yes

Octafluoro-1-butene (FEP)
CASRN: 360-89-4
DESC. Gas

Octafluorocyclobutane; Perfluorocyclobutane (FEP, TEF)
CASRN. 115-25-3
DESC: Gas

Octafluoroisobutylene; Perfluoroisobutylene (FEP, TEF)
CASRN: 382-21-8

Octyl alcohol; 1-Octanol (NEO)
CASRN: 111-87-5
DESC: Semivolatile Liquid
SKIN IRR: Mild
INGES ACUTE: Mouse LD_{50}: 1790 mg/kg

Palmitic acid (NEO)
CASRN: 57-10-3
DESC. Solid, m.p 61-64°C

MONS 020580

SKIN IRR: Human: 75 mg/3 days, mild
TUMORIGEN: Mouse (implant) TD_{Lo}: 1000 mg/kg
IVN: Mouse LD_{50}: 57 mg/kg

Pentachlorobenzene (PCP)
CASRN: 608-93-5
DESC. Solid, m.p. 86°C
ORAL: Rat LD_{50}: 1080 mg/kg

1,4-Pentadiene (PE)
CASRN: 591-93-5
DESC: Liquid/Gas (b.p. 26°C)

Pentane (EPO, PE)
CASRN: 109-66-0
STDS: OSHA: 1000 ppm, 2950 mg/m³
TLV: 500 ppm, 1300 mg/m³ TWA; 750 ppm, 2250 mg/m³ STEL
DESC: Volatile Liquid
HLTH: Flammable (18, Less than 3000 ppm).
Narcosis (8, Greater than 3000 ppm).

2-Pentanone (PE)
CASRN: 107-87-9
STDS: OSHA: 200 ppm, 700 mg/m³
TLV: 200 ppm, 700 mg/m³ TWA; 250 ppm, 875 mg/m³ STEL
DESC: Volatile Liquid
HLTH: Irritation-Eyes, Nose, Throat--Moderate (15, Less than 400 ppm).
Narcosis (8, Greater than 400 ppm).

1-Pentene (CSPE, PE)
CASRN: 109-67-1
DESC. Liquid/Gas (b.p. 29.9-30.1°C)

Perylene [a PAH] (CRE)
CASRN: 198-55-0
DESC: Solid, m.p. 227-279°C
MUTAGEN

Phenanthrene [a PAH] (CRE, CSPE, PE, STY)
CASRN: 85-01-8
DESC: Solid, m.p. 99-101°C
INGES ACUTE: Mouse LD_{50}: 700 mg/kg

Phenol (CRE, EPO, KAP, NOM, STY, SUL, XLPE)
CASRN: 108-95-2
STDS. OSHA: 5 ppm, 19 mg/m³
TLV. 5 ppm, 19 mg/m³ TWA; 10 ppm, 38 mg/m³ STEL
DESC. Solid, m.p. 40.5-41.5°C (absorbs water from air and liquefies)

HLTH. Irritation-Eyes, Nose, Throat, Lungs--Marked (14).
Acute and chronic systemic toxicity (4)
Suspect carcinogen (2).
SKIN IRR: Severe
SKIN ABS Yes
INGES ACUTE. Human LD_{Lo}: 140 mg/kg

Phenylacetaldehyde; α-Tolualdehyde; Benzeneacetaldehyde (STY)
CASRN. 122-78-1
DESC: Semivolatile Liquid
SKIN IRR: Human: 2%/48 H
ORAL Rat LD_{50}: 1550 mg/kg

1,3-Phenylenediamine; 1,3-Diaminobenzene (NOM)
CASRN: 108-45-2
DESC. Volatile Liquid
IARC CARC. Animal Indefinite, '78
TUMORIGEN: Rat TD_{Lo}, scu. 1485 mg/kg
ORAL: Rat LD_{50}: 650 mg/kg

m-Phenylenediisocyanate; 1,3-Diisocyanatobenzene (NOM)
CASRN 123-61-5
DESC. Solid?
IVN: Mouse LD_{50}: 5.6 mg/kg

2,3-o-Phenylenepyrene; Indeno[1,2,3-cd]pyrene [a PAH] (CRE)
CASRN. 193-39-5
DESC: Solid
MUTAGEN
IARC CARC. Animal Positive '73.

Phenyl Isocyanate (KAP)
CASRN: 103-71-9
DESC: Semivolatile Liquid
SKIN ABS. Rabbit LD_{50}: 7130 mg/m³
INGES ACUTE. Rat LD_{50}: 940 mg/kg

2-Phenylnaphthalene (PE)
CASRN: 612-94-2
DESC: Semivolatile liquid

N-Phenyl-2-naphthylamine (NEO)
CASRN 135-88-6
DESC Solid, m.p. 107-109°C
HLTH IARC CARC. Animal Suspect, '78
IARC CARC Human Indefinite, '78.
Metabolizes to 2-naphthylamine in humans and animals
INGES ACUTE Rabbit LD_{Lo} 1000 mg/kg

Phenyl p-tolyl ether (SUL)
CASRN: 1706-12-3

Phthalanil (NEO)
CASRN: 520-03-6

Phthalates (XLPE)

Phthalic anhydride (NEO)
CASRN: 85-44-9
DESC: Solid, m.p. 132-134°C
STDS: OSHA: 2 ppm, 12 mg/m^3
TLV: 1 ppm, 6 mg/m^3 TWA; 4 ppm, 24 mg/m^3 STEL
HLTH: Irritation-Eyes, Nose, Throat, Lungs--Marked (14).
Asthma (9).
Contact skin irritant and sensitizer (3).
SKIN IRR: Yes, severe
INGES ACUTE: Guinea pig LD_{50}: 100 mg/kg

Phthalimide (KAP)
CASRN: 85-41-6
DESC: Solid, m.p. 234-236°C
ORAL: Mouse LD_{50}: 5000 mg/kg

Polystyrene combustion products (800°C) (STY)
INL: Mouse LC_{50}: 120 mg/m^3/10 min

Polytetrafluoroethylene decomposition product (TEF)
CASRN: 9002-84-0
STDS: TLV: 81 (Polytetrafluoroethylene decomposition product)
DESC: Variable
HLTH: Acute toxic effects (Polymer fume fever) (4)
IARC CARC: Animal Positive, '79
IARC CARC: Human Indefinite, '79.

Polyurethane A combustion products (PU)
INL: Mouse LC_{50}: 38 mg/m^3/10 min

Polyurethane thermal decomposition products (PU)
MUTAGENIC

Propane (EPO, PE, PU)
CASRN: 74-98-6
STDS OSHA: 1000 ppm, 1800 mg/m^3
DESC Gas
HLTH: Explosive (18)
CNS effects (7).
Asphyxiant (17).
ACGIH: E (Simple asphyxiant)

Propionaldehyde; Propanal (PE, PU)
CASRN: 123-38-6
DESC: Volatile Liquid
SKIN IRR: Mild
INGES ACUTE: Rat LO_{50}: 800 mg/kg

Propionic acid (PE)
CASRN: 79-09-4
STDS: TLV-TWA: 10 ppm, 30 mg/m³
STEL: 15 ppm, 45 mg/m³
DESC: Semivolatile Liquid
ORAL: Rat LO_{50}: 2500 mg/kg
SKIN: Rabbit LD_{50}: 500 mg/kg
SKIN IRR: Rabbit: 495 mg, open, savere

Propionitrile; Ethyl cyanide (PU)
CASRN: 107-12-0
STDS: Criteria Document Recommended Exposure: 14 mg/m³ TWA
DESC: Volatile Liquid
EYE IRR: Rabbit: 20 mg
ORAL: Rat LD_{50}: 39 mg/kg

Propyl alcohol; Propanol (PU)
CASRN: 71-23-8
STDS: OSHA: 200 ppm, 500 mg/m³
TLV: 200 ppm, 500 mg/m³ TWA; 250 ppm, 625 mg/m³ STEL
DESC: Volatile Liquid
HLTH: Irritation-Eyes, Nose, Throat--Mild (16).
Narcosis (8).
Suspect carcinogen (2).
SKIN IRR: Mild
SKIN ABS: Yes
INGES ACUTE: Rebbit LD_{Lo}: 3500 mg/kg

n-Propylbenzene (see also Cumene) (STY)
CASRN: 103-65-1
DESC: Semivolatile Liquid
INGES ACUTE: Rat LD_{50}: 4830 mg/kg

Propylene; 1-Propene (CSPE, EPO, NOM, PE, PET, PU)
CASRN: 115-07-1
TLV: Asphyxiant
DESC: Gas

Propyne; Methylacetylene (PE, PU)
CASRN: 74-99-7
STDS: OSHA: 1000 ppm, 1650 mg/m³
TLV: 1000 ppm, 1650 mg/m³ TWA; 1250 ppm, 2040 mg/m³ STEL
DESC Gas
HLTH. Explosive (18, Less than 2000 ppm).
Narcosis (8, Greater than 2000 ppm).

MONS 020584

Pyrene [a PAH] (CRE, PE, STY)
CASRN: 129-00-0
DESC: Solid, m.p. 149-151°C
SKIN IRR: Moderate

Pyridine (PU)
CASRN: 110-86-1
STDS: OSHA: 5 ppm, 15 mg/m³
TLV: 5 ppm, 15 mg/m³ TWA, 10 ppm, 30 mg/m³ STEL
DESC: Volatile Liquid
HLTH: Cumulative liver, kidney and bone marrow damage (3).
CNS effects (7).
SKIN IRR: Mild
SKIN ABS: Rabbit LD_{50}: 1121 mg/kg

Pyrrole (PU)
CASRN: 109-97-7
DESC: Semivolatile Liquid
SCU: Mouse LD_{50} 61 mg/kg
IPR: Rabbit LD_{Lo}: 150 mg/kg

Quinoline (CRE, PU)
CASRN: 91-22-5
DESC: Semivolatile Liquid
MUTAGEN
SKIN IRR: Rabbit: 10 mg/24 H, mild
EYE IRR: Rabbit: 0.250 mg, severe
ORAL: Rat LD_{50}: 331 mg/kg
SKIN: Rabbit LD_{50}: 540 mg/kg

Silicon fluoride; Silicon tetrafluoride, Tetrafluorosilane (FEP, TEF)
CASRN: 7783-61-1
STDS: OSHA. 2.5 mg (HF)/m³ TWA (for hydrolysis product)
TLV: 2.5 mg (HF)/m³ TWA
DESC: Gas

Squalene (NEO)
CASRN: 111-01-3
DESC: Semivolatile Liquid

Styrene (CSPE, EPO, NIT, PET, PU, STY, SUL)
CASRN: 100-42-5
STDS: OSHA: 100 ppm
TLV: 50 ppm, 215 mg/m³ TWA; 100 ppm, 425 mg/m³ STEL
DESC: Semivolatile Liquid
HLTH: Irritation-Eyes, Nose, Throat--Moderate (15).
CNS effects (7).
Narcosis (8)
Mutagen (2).
IARC CARC: Animal Positive, '79.
IARC CARC: Animal Suspected, '82.

IARC CARC: Human Indefinite, '79
IARC CARC: Human Suspected, '82.
SKIN ABS: Yes
SKIN IRR: Moderate
INGES ACUTE: Mouse LD_{50}: 316 mg/kg

Sulfur dioxide (CSPE, NEO, SUL)
CASRN: 7446-09-5
STDS: OSHA: 5 ppm, 13 mg/m³
TLV: 2 ppm, 5 mg/m³ TWA; 5 ppm, 10 mg/m³ STEL
DESC: Gas
HLTH Irritation-Eyes, Nose, Throat, Lungs--Marked (14).
Bronchoconstriction (4).
Mutagen (2)
Suspect reproductive effects (5)

Terephthalic acid (PET)
CASRN: 100-21-0
DESC. Solid, m.p. > 300°C

Tetrachlorodibenzo-p-dioxin; TCDD (PCP)
DESC Solid
CASRN: (1,2,3,4-isomer) 30746-58-8; (1,2,3,8-isomer) 53555-02-5;
(1,3,6,8-isomer) 33423-92-6; (1,3,7,8-isomer) 50585-46-1;
(2,3,6,7-isomer) 34816-53-0
IARC CARC: Animal Indefinite, '77.
2,3,7,8-isomer
CASRN: 1746-01-6
EYE IRR: Rabbit: 2 mg, Moderate
TERATOGEN
MUTAGEN
ORAL: Rat LD_{50}: 22.5 µg/kg
IARC CARC: Animal Indefinite, '77
NTP/NCI CARC. Positive in mice and rats, '82.

Tetrafluoroethylene; Tetrafluoroethene (FEP, TEF, TFZ)
CASRN. 116-14-3
DESC. Gas
IHL Rat LC_{50}: 40,000 ppm/4 H

Tetrahydrofuran (PE)
CASRN: 109-99-9
STDS. OSHA. 200 ppm, 590 mg/m³
TLV: 200 ppm, 590 mg/m³ TWA; 250 ppm, 735 mg/m³ STEL
DESC Volatile Liquid
HLTH Irritation-Eyes, Nose, Throat, Skin--Moderate (15).
Narcosis (8) Mutagen (2).
INGES ACUTE Rat LD_{Lo} 3000 mg/kg

2,3,5,6-Tetramethylphenol (CRE)
CASRN 527-35-5

SKIN IRR: Yes, Sensitization also
INGES ACUTE: Rat LD_{50}: 800 mg/kg

Formic acid; Methanoic acid (PE, STY)
CASRN: 64-18-6
STDS: OSHA: 5 ppm, 9 mg/m³
TLV: 5 ppm, 9 mg/m³ TWA
DESC: Volatile Liquid
HLTH: Irritation-Eyes, Nose, Throat, Skin, Lungs--Marked (14).
Mutagen (2)
SKIN IRR: Yes, if concentrated
INGES ACUTE: Rat LD_{50}: 1100 mg/kg

Furan (PE)
CASRN: 110-00-0
DESC: Volatile Liquid
IHL: Mouse LC_{50}: 120 mg/m³/1H
IPR: Mouse LD_{50}: 7 mg/kg
IPR: Rat LD_{50}: 5.2 mg/kg

Heptachlorodibenzo-p-dioxin (PCP)
CASRN: 37871-00-4; (1,2,3,4,6,7,8-isomer) 35822-46-9
IARC CARC: Animal Indefinite, '77.

n-Heptacosane (NED)
CASRN: 593-49-7
DESC: Solid, m.p. 59-61°C

1-Heptene (PE)
CASRN: 592-76-7
DESC: Volatile Liquid

Hexachlorobenzene (PCP)
CASRN: 118-74-1
DESC: Solid
HLTH: IARC CARC: Animal Positive, '79.
IARC CARC: Human Suspect, '79.

Hexachlorodibenzo-p-dioxin (PCP)
CASRN: 34465-46-8
DESC: Solid, m.p. 227-229°C
EYE IRR: Rabbit: 2 mg, moderate
ORAL: Rat TD_{Lo}: 100 mg/kg
ORAL: Mouse LD^{Lo}_{50}: 1.25 mg/kg
IARC CARC: Animal Indefinite, '77 (but a 2:1 mixture of the 1,2,3,7,8,9- and 1,2,3,6,7,8-isomers was a carcinogen in rats and mice).

Hexachlorodibenzofuran (PCP)
CASRN 55684-94-1

MONS 020572