IH Aspects of Thermal Degradation Products

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Presentation Overview

- Background information/emerging issues of Thermal Degradation Products (TDPs)
- Information gaps
- Definitions
- Case studies/material examples
- Exposure assessment
- Looking ahead

This presentation is NOT...

- A review of Fire Science
- A treatise on engineering controls
- An outline of specific methodologies for laboratory/ analytical testing methods
- An expression of opinions on behalf of any manufacturers of materials cited as case examples

Background/Emerging Issues

- When you heat most materials past a certain point….
  - – new species of air contaminants arise, typically orders of magnitude more toxic than the “parent” material
  - – air contaminants may change phase (e.g. particulates instead of vapors/gases

Background/Emerging Issues

- New chemistries/new industrial processes
- Polymers heated past degradation points
- More emphasis among manufacturers on “Life Cycle Management” and “Product Responsibility/Stewardship”

Background/Emerging Issues

- Many legal cases have been brought based on lack of information and/or consideration of thermal degradation products
- Exposure issues RE thermal decomposition products have been studied more extensively in Scandinavia

Definitions (ASTM)

- Pyrolysis - irreversible chemical decomposition caused by heat, usually without oxidation
- Combustion - a chemical process of oxidation that occurs at a rate fast enough to produce temperature rise, and usually light, either as a glow or flame
- Fire - destructive burning as manifested by any or all of the following: light, flame, heat, smoke

Definitions (ASTM)

- Today, we will focus on:
  - **Pyrolysis**
  - Combustion
  - Fire

More on Pyrolysis...

- More in-depth definition: "...a process, by which a solid (or a liquid) undergoes degradation of its chemicals into smaller volatile molecules under heat, without interaction with oxygen or any other oxidants, that is necessary for almost all solids (or liquids) to burn."

Pyrolysis Basics

1. Decomposition of a material into simpler compounds by the action of heat alone.
2. The pyrolysis process does not imply a reaction between an oxidant and a reducing agent. It is merely decomposition of a material subjected to heating, without involving any other substances.

Pyrolysis Basics

3. The more heat that is provided (energy transferred), the faster the pyrolysis will occur and eventually, if an oxidant (oxygen) is present in the correct proportion, a flaming fire will result.
4. The only solids that do not undergo pyrolysis prior to burning are the solids that undergo sublimation.

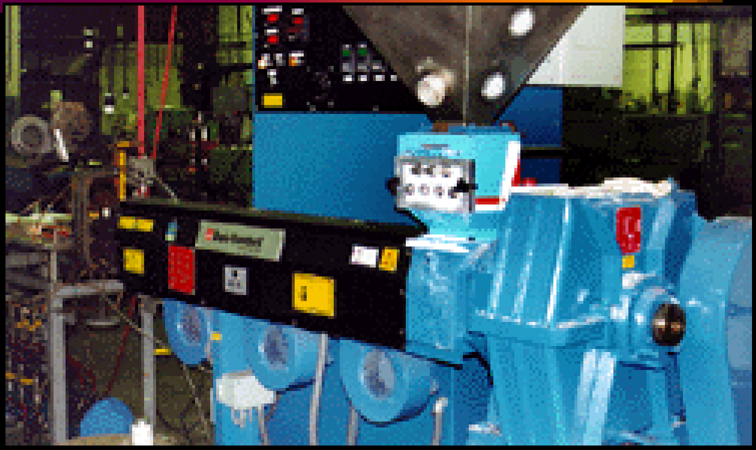
Information Gaps

- Thermal degradation products may be synergists to other existing air contaminants in the workplace atmosphere
- VERY few manufacturers conduct toxicity testing on thermal degradation products of their “parent” materials
- MSDSs authors routinely ignore or incorrectly characterize thermal degradation products

Risk Evaluation

- Laboratory studies - headspace analyses, thermogravimetric analyses (TGAs)
- Ideally, a manufacturer should test samples as used by a customer or industrial user - e.g. including all coatings, adhesives, etc.
- Evaluate both “normal” use scenario, and abuse scenario
- Test at a wide range of temperatures to determine variance in TDPs

Risk Evaluation -
Some industrial processes



- Fabrication
- Extrusion
- Injection molding
- Laser Cutting
- Lamination
- Waste disposal - e.g. incineration
- Changes in manufacturing processes, specifically those involving heat

Predicting Thermal Degradation Products

Some basics of predicting TDPs

- Organic materials - *nearly always* ⟶ CO, CO_2
- Nitrogen based materials ⟶ NH_3, NOx, HCN^-
- Chlorine based materials ⟶ HCl, Cl2, phosgene
- Sulfur based materials ⟶ SO2
- Fluorine based materials ⟶ HF

Some basics of predicting TDPs - Plastics

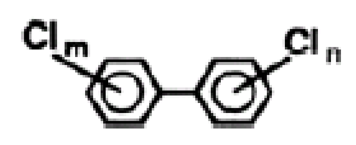
- Polypropylene (@270°C) ⟶ dimethylheptene
- Polystyrene (@280°C) ⟶ styrene
- Polyvinylchloride (@250°C) ⟶ HCl
- (polyethylene will be described in more depth in a later case study)

Some basics of predicting TDPs - Miscellaneous materials

- Acrylic (polyacrylonitrile)/nylon fibers → HCN^-, acrylonitrile
- Polyester → benzene, benzoic acid
- Polyolefin → acrolein
- Cellulose → 175 different organic compounds - (demonstrates complexity of evaluation)

Historical Examples

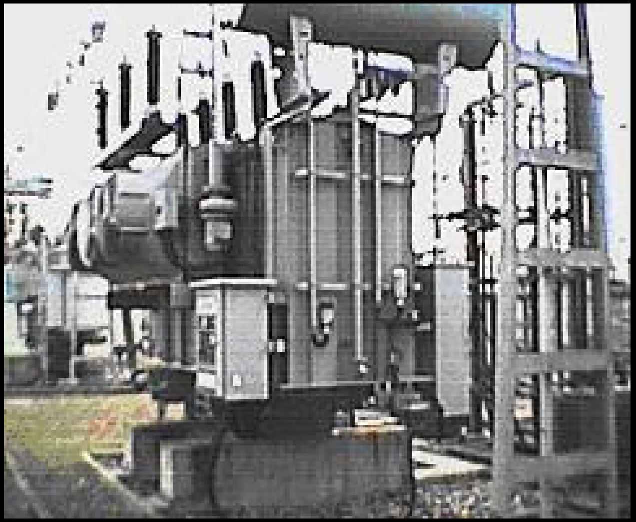
Historical Example - PCBs



- Under pyrolytic conditions, PCBs (polychlorinated biphenyls) can be converted to PCDFs (polychlorinated dibenzofurans)
- PCDFs are orders of magnitude more toxic than PCBs
- Fires involving PCBs should always be evaluated for PCDF contamination prior to establishing necessary cleanup measures

Historical Example - PCBs

- If dichlorbenzenes are also present (was common in *Askarel* products) can be converted to even more toxic PCDDs (polychlorinated dibenzodioxins)

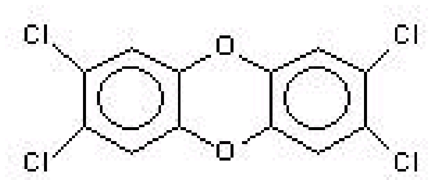


Historical Example - PCBs

- 1981- State Office Building in NY - fire in basement mechanical room
- 750 litres of *Askarel* leaked from a transformer and caught fire.
- Pyrolysis of the *Askarel* led to the formation of a fine oily soot that spread throughout the building via 2 ventilation shafts.

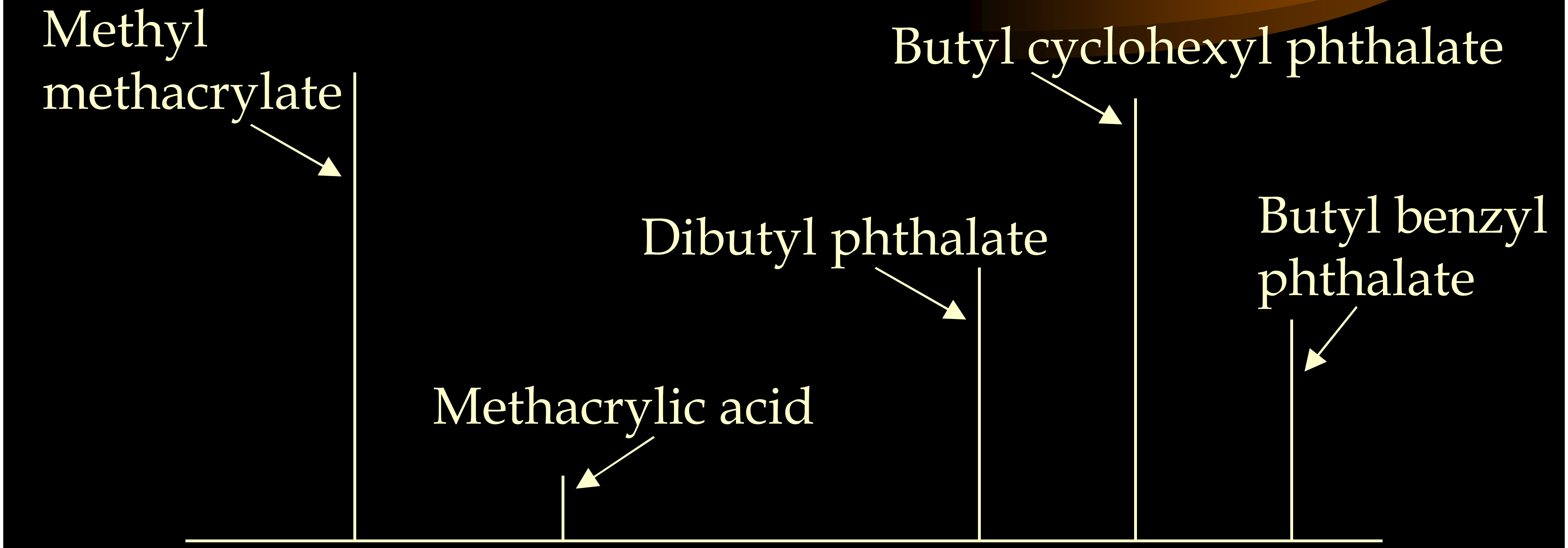
Historical Example - PCBs

- Several days after the fire:
- The average air concentration of PCBs in the building = 1.5 $\mu g/m^3$
- Soot samples were analysed:
- average levels of 3 mg TCDD/kg and 199 mg 2,3,7,8-TCDF/kg



2,3,7,8-TCDD

Forensic Example - Auto Paints



Methyl methacrylate

Butyl cyclohexyl phthalate

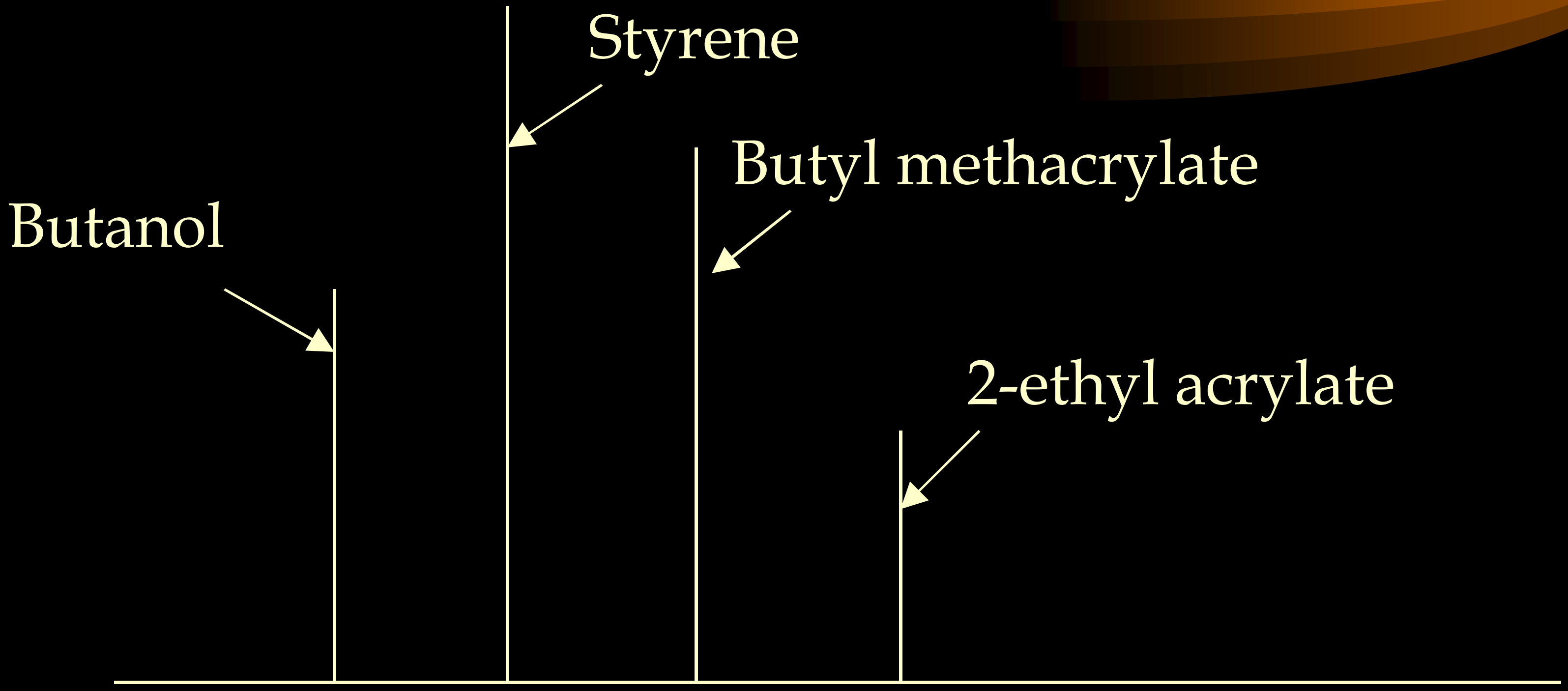
Dibutyl phthalate

Butyl benzyl phthalate

Methacrylic acid

Chromatograph of Acrylic Lacquer (GM)

Forensic Example - Auto Paints



Styrene

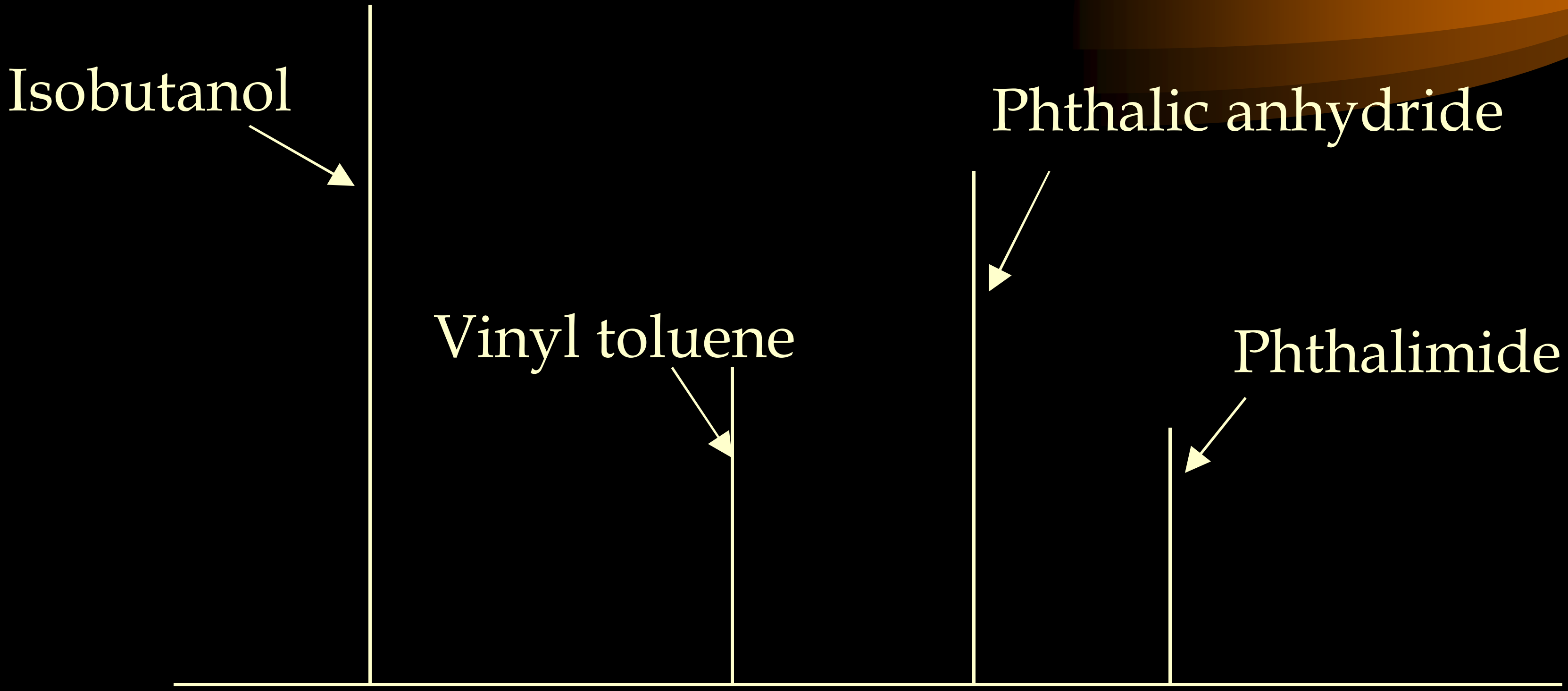
Butyl methacrylate

Butanol

2-ethyl acrylate

Chromatograph of Acrylic Enamel (Ford)

Forensic Example - Auto Paints



Isobutanol

Vinyl toluene

Phthalic anhydride

Phthalimide

Chromatograph of Alkyd Enamel (Honda)

Product Example - PTFE

- Polytetrafluoroethylene - Teflon®
- One of the earliest examples of thorough evaluation of TDPs - 1975 (!)
- Mold filled with resin granules, compacted, heated to 300°C for several minutes - forms a rigid mass (sintering)
- Studies were undertaken to determine the temperatures and types of toxicants evolved from PTFE

Variables considered in TDP exposure characterization

- Air flow rate and volume over the sample while heating
- Relative humidity of the air
- Sample size
- Surface area

Laboratory Testing

- Off-gases analyzed by a gas chromatographic procedure
  - tetrafluoroethylene (TFE) at 450°C.
  - hexafluoropropylene (HFP) at 460°C
  - perfluoroisobutylene (PFIB) at 475°C
- Other gaseous products
  - hydrogen fluoride
  - carbonyl fluoride
  - fluorinated hydrocarbons

Toxicity of off-gases

- Approximate lethal concentrations (ALC):
  - TFE - 45,000 ppm
  - HFP - 3000 ppm
  - Perfluoroisobutylene (PFIB) - 0.5 ppm
- Polymer-fume fever
- Symptoms similar to metal fume fever
- Poorly understood mechanism of toxicity - likely involves ultrafine particles

Conclusions

- Safe to sinter PTFE at 300°C
- Ventilation and respirators would provide adequate protection in the event of any overheating; at least at temperatures up to approximately 500°C.
- > 500°C. would require closed, ventilated system

Industrial Processing Examples

Industrial Example - Polyurethane Materials

- Polyurethane foams (PUFs)
- Polyurethane plastics (PURs)
- Based on TDI or MDI chemistry
- Studies found that thermal degradation @ 300° - 350°C forms TDI and MDI monomer
- Particulate phase for TDI "parent" is only 3%, but MDI is 75% (!)

Polyurethane Materials - Examples

- Study of car repair shops
  - grinding, cutting, welding of painted metal sheets
  - relatively low amounts of MDI vapor released - 4 $\mu g/m^3$
  - BUT, high concentrations of ultrafine MDI particles (0.05 μm to 0.2 μm)

Epidemiological Study - Nylon Flocking

- Short fibers (flock) are cut from cables of parallel synthetic monofilaments (tow) and applied (flocked) to an adhesive-coated substrate
- Followed by heat curing
- The nylon manufacturer's MSDS stated: "*As shipped, Nylon Polyamide Fiber products do not pose a hazard. Under normal conditions of use, Nylon Polyamide Fiber does not generate respirable fibers or dust.*"

Nylon Flocking

- “Flock worker's lung”
  - persistent respiratory symptoms
  - previous work in the flocking industry, and;
  - histologic evidence of interstitial lung disease

Nylon Flocking

- Nylon 6,6 melts at approximately 260°C
- At higher temperatures, can produce:
  - ammonia
  - various amines
  - hydrogen cyanide
  - nitrogen dioxide

Nylon Flocking

- Exposure confounders:
- Potato starch and tannic acid, two constituents of the finish
- Airborne bacterial endotoxin
- Potato antigens

Industrial Example- Polyethylene Processing

- *Injection molding - PE* is melted and injected into a mold where it hardens.
- *Blow molding* - a tube is extruded vertically downwards onto a spigot. The mold halves close on to the extrudate (‘parison’) and air is blown through the spigot so that the parison takes the shape of the mold.

Polyethylene Processing

- *Extrusion* - granular PE is metered into a heated barrel or cylinder, in which a rotating screw moves up the granules, which are compacted and plasticized. The melt is then forced through an orifice to give a product of constant cross section.

Polyethylene Processing

- Typical processing temperatures
- Extrusion (pipes): 140 – 170 ºC
- Films and coatings: 200 – 340 ºC
- Injection molding: 150 – 370 ºC
- Welding or thermocutting - may be significantly higher temperatures than above mentioned processing applications.

Polyethylene Processing

- Laboratory simulations using degradation temperatures close to those in industrial processing identified following major components:
- formaldehyde
- formic acid
- acetaldehyde
- acetic acid

Polyethylene Processing

- To show the complexity of TDPs - at processing temps of 264 – 289 °C the following minor components were identified (!):

Alkoxy radicals
Acrolein
Propionic acid
Heptane
Acrylic acid
Octene
Butyric acid
Octane
Isovaleric acid
Methanol
Hydroxyvaleric acid
Ethanol
Crotonic acid
Furan
Caproic acid
Tetrahydrofuran
Butyrolactone
Formaldehyde
Valerolactone
Acetaldehyde
Hydroperoxides
Propanol
Butene
2–Pentanone
Butane
2–Hexanone
Pentene
2–Heptanone
Hexene
Formic acid
Hexane
Acetic acid
Heptene
Butanal
Isobutanal
Ethene
Pentanal
Propene
Acetone
Propane
Methyl vinyl ketone
Cyclopropane
Methyl ethyl ketone

Polyethylene Processing

- During processing of polyethylene
- Highest measured concentration (mg/m3)
- Formaldehyde = 0.2
- Acetaldehyde = 0.4
- Formic acid = 2.1
- Acetic acid = 4.9
- But…confounder - aerosols resembling paraffin

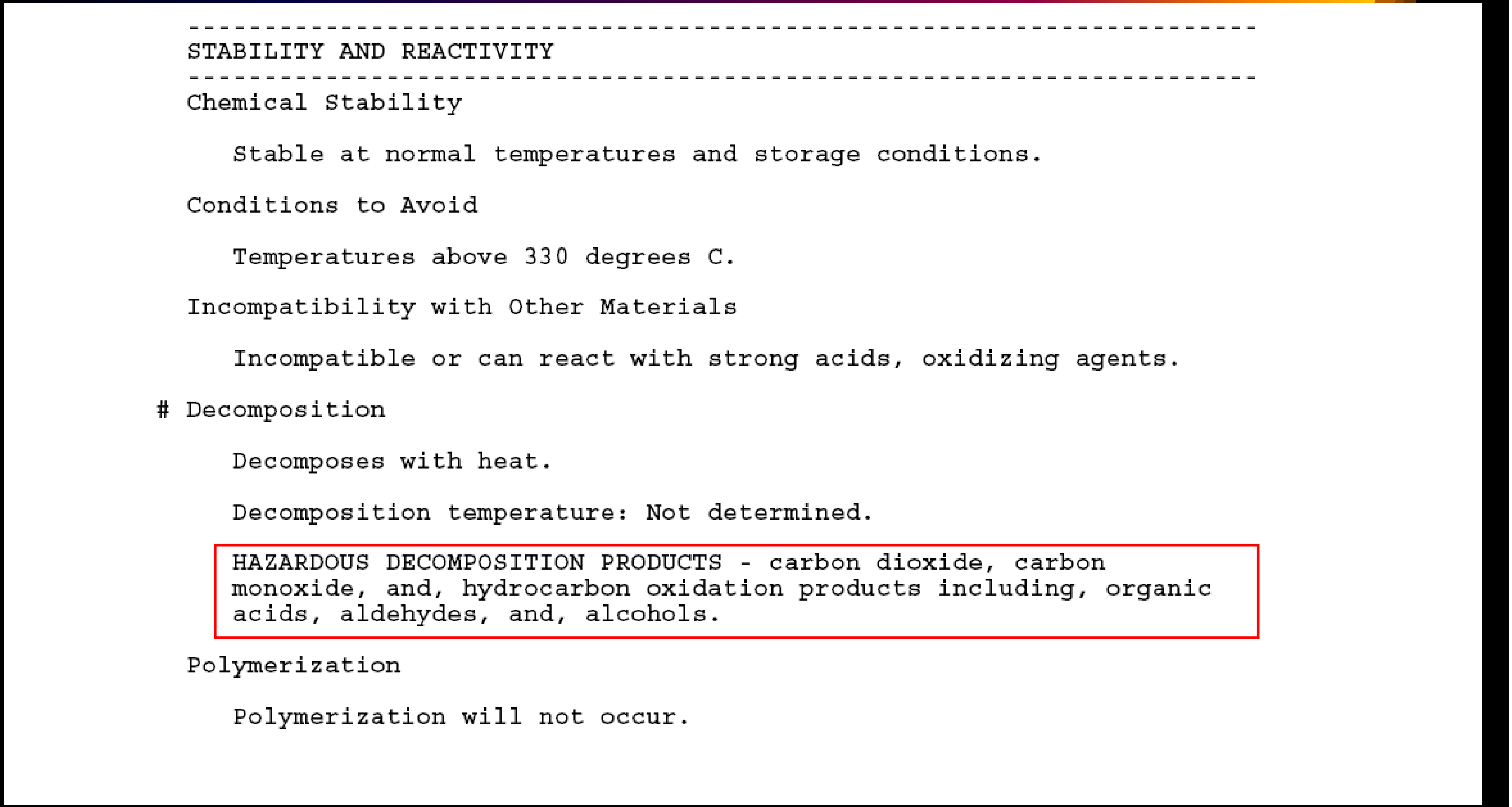
New Technologies - Plasma Cutting

- Process that uses a high velocity jet of ionized gas that is delivered from a constricting orifice to cut through metals
- While cutting through mild steel, primary contaminants:
  - nitrogen dioxide
  - formaldehyde
  - ozone

Product Example - MSDSs and Risk Evaluation

- Assume you’re going to initiate a new hot process involving an acrylic copolymer
- You can buy the material from 4 different manufacturers
- Let’s look at their MSDSs….

MSDS - Large Manufacturer



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  STABILITY AND REACTIVITY
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  Chemical Stability

     Stable at normal temperatures and storage conditions.

  Conditions to Avoid

     Temperatures above 330 degrees C.

  Incompatibility with Other Materials

     Incompatible or can react with strong acids, oxidizing agents.

# Decomposition

     Decomposes with heat.

     Decomposition temperature: Not determined.

     HAZARDOUS DECOMPOSITION PRODUCTS - carbon dioxide, carbon
     monoxide, and, hydrocarbon oxidation products including, organic
     acids, aldehydes, and, alcohols.

  Polymerization

     Polymerization will not occur.
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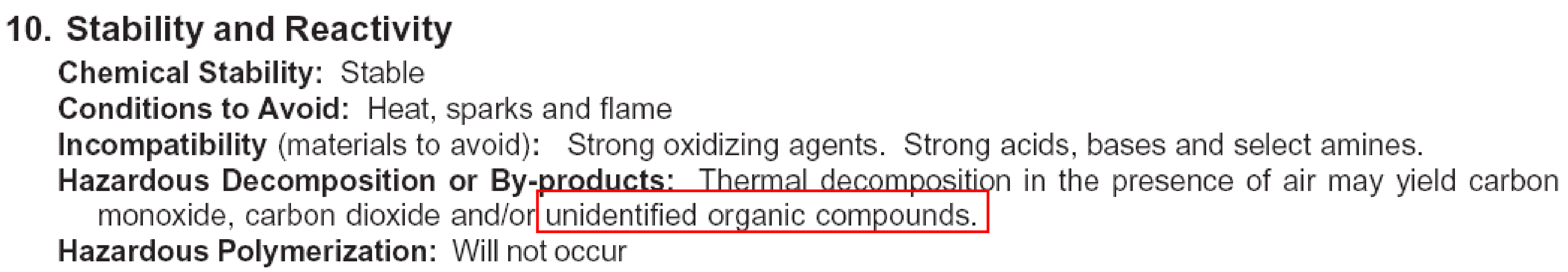
MSDS - Medium Manufacturer



10. Stability and Reactivity

Chemical Stability: Stable

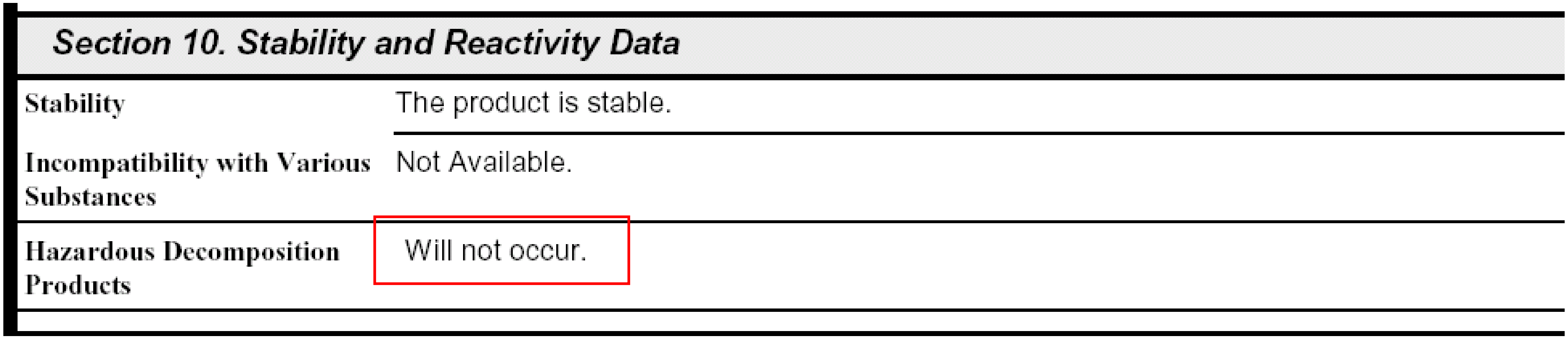
Conditions to Avoid: Heat, sparks and flame

Incompatibility (materials to avoid): Strong oxidizing agents. Strong acids, bases and select amines.

Hazardous Decomposition or By-products: Thermal decomposition in the presence of air may yield carbon monoxide, carbon dioxide and/or unidentified organic compounds.

Hazardous Polymerization: Will not occur

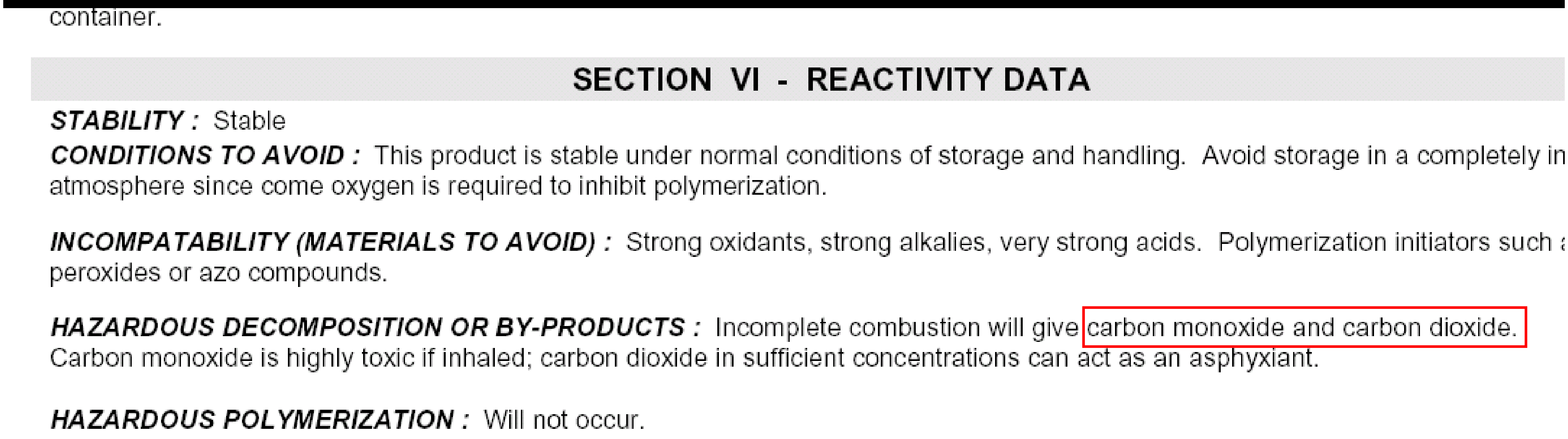
MSDS - Specialty Supplier



Section 10. Stability and Reactivity Data

Stability	The product is stable.
Incompatibility with Various Substances	Not Available.
Hazardous Decomposition Products	Will not occur.

MSDS - Bulk Chemical Supplier



container.

SECTION VI - REACTIVITY DATA

STABILITY : Stable

CONDITIONS TO AVOID : This product is stable under normal conditions of storage and handling. Avoid storage in a completely in atmosphere since come oxygen is required to inhibit polymerization.

INCOMPATABILITY (MATERIALS TO AVOID) : Strong oxidants, strong alkalies, very strong acids. Polymerization initiators such peroxides or azo compounds.

HAZARDOUS DECOMPOSITION OR BY-PRODUCTS : Incomplete combustion will give carbon monoxide and carbon dioxide. Carbon monoxide is highly toxic if inhaled; carbon dioxide in sufficient concentrations can act as an asphyxiant.

HAZARDOUS POLYMERIZATION : Will not occur.

Product Example - Circuit board overheating

- Environmental chamber, over approximately 30 second period
- Metals:
  - tin = 900 ug/m^3
  - lead = 750 ug/m^3
- Acid gases
  - 85 mg/m^3
  - 2 mg/m^3

Conclusions and Future Directions

- Developing processing methods that allow lower temperatures, hence fewer TDPs - e.g. “Squeeze”/pressure methods for plastics molding
- MSDS quality initiatives may result in more complete information on TDPs

Conclusions and Future Directions

- More formal evaluation methods - e.g. TGA (thermogravimetric analysis) can predict when molecules will begin to “unzip”
- Inhalation toxicity testing of complex mixtures, especially ultrafine particles