

DuPont Overview of Fluoropolymers, C-8 and PARKVIEW Operations Parkersburg,

Presented to the State of Ohio Environmental Protection Agency

February, 2000
Columbus, Ohio

ASH028132

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Agenda

- Benefits of Fluoropolymers, Role of C-8 and Research on C-8 Alternatives
- APFO Toxicology Review
- DuPont Stewardship Efforts
- Multi-Media Consent Order w/ WVDEP

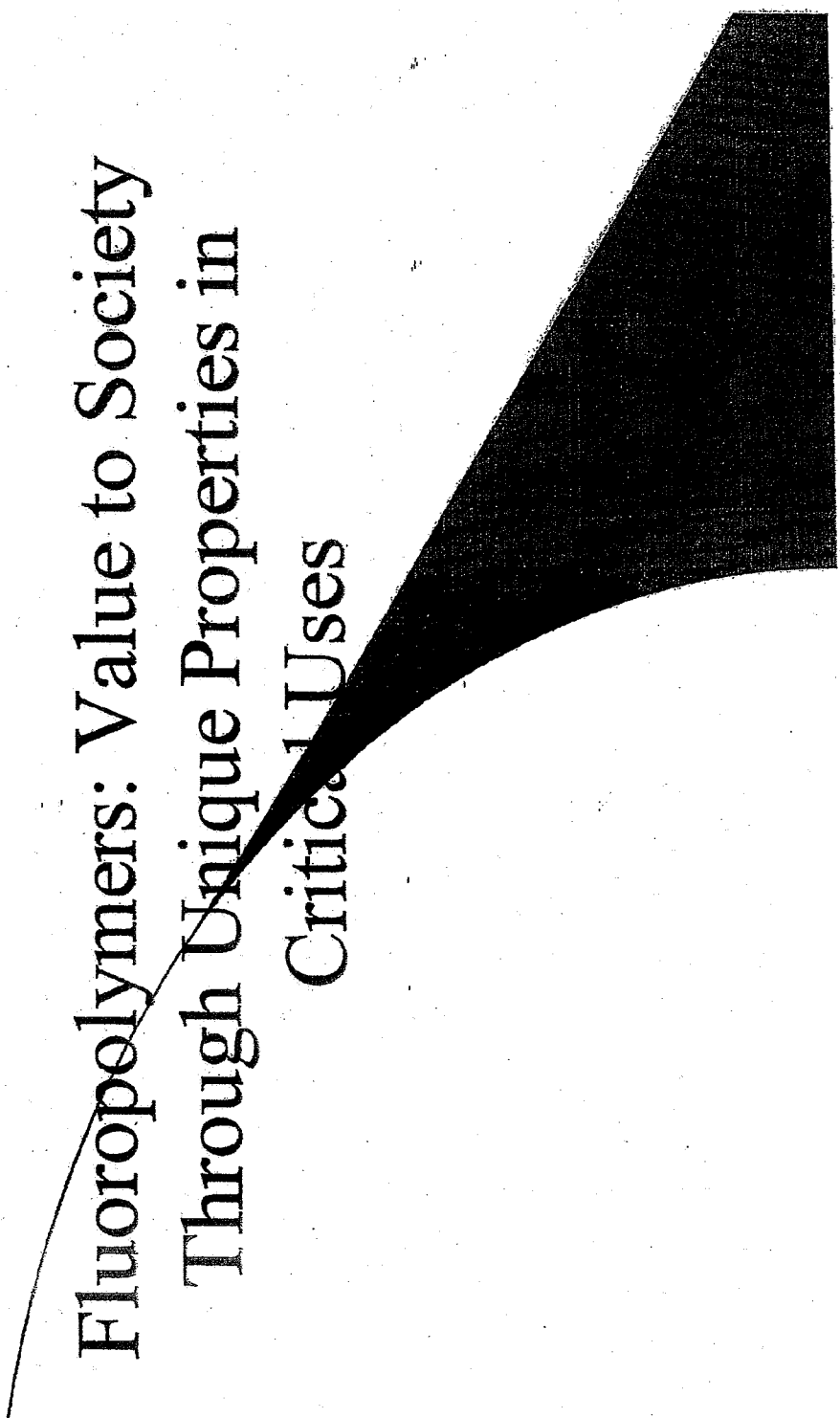
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Fluoropolymers: Value to Society Through Unique Properties in Critical Uses



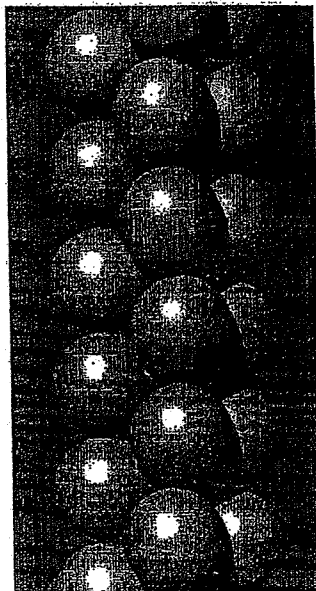
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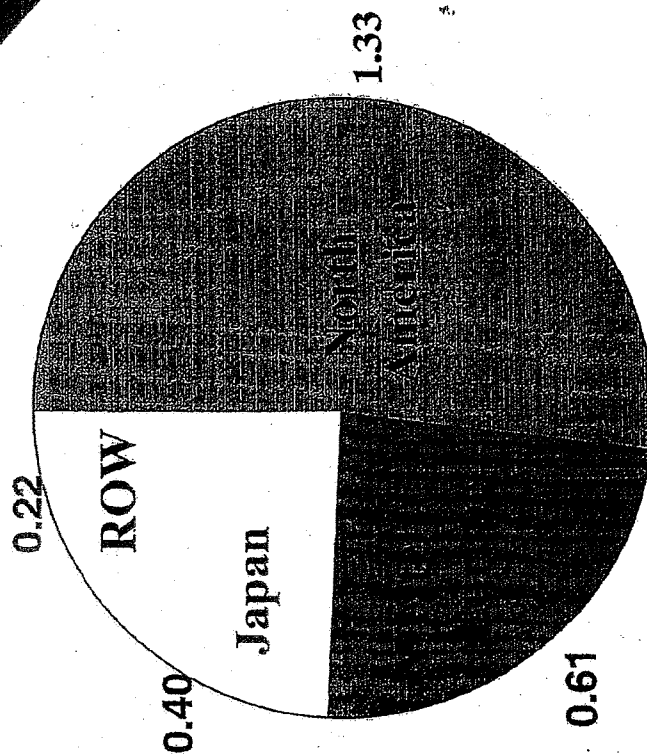
Fluoropolymers: "Super" Polymers

- Chemical resistance across broad temperature range
- "Slipperiest" substance known to man
- Unique properties/High value in use



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Fluoropolymers – 2000 Global Market Demand (\$Billions)



Total Demand \$2.5 billion
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Major Industries Served by Fluoropolymers/elastomers

- Aerospace/Military
- Automotive/Transportation
- Chemical/Petrochemical Processing
- Semiconductor/Electronics Manufacturing
- Telecommunications
- Power Generation/Pollution Control
- Consumer Housewares

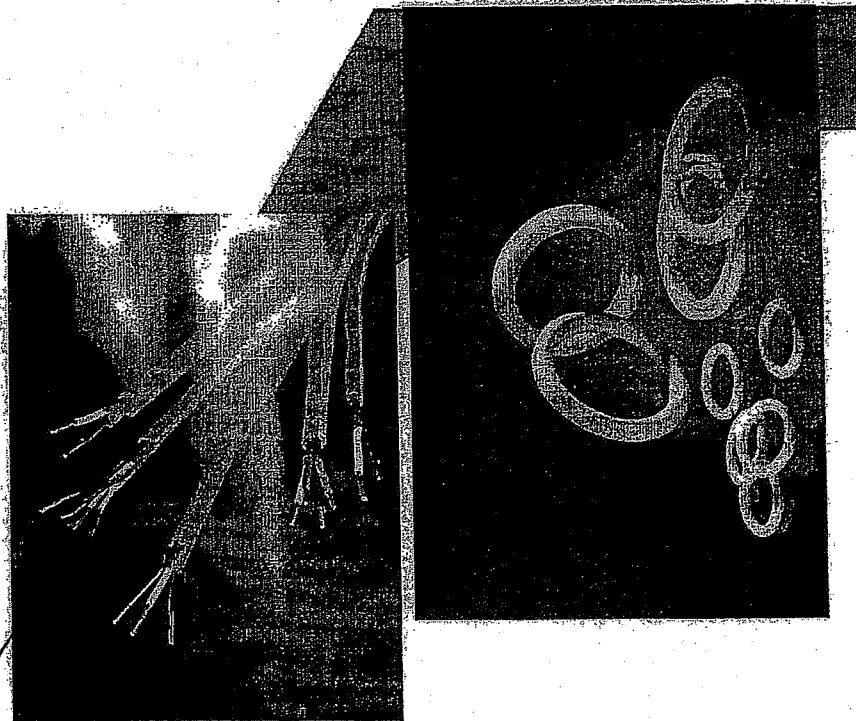
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Aerospace/Military



Key requirements: Temperature and chemical resistance; electrical performance; low flammability

Major uses:

Wire and cable insulation

Fuel and hydraulic hoses

Seals/bushing

Space apparel

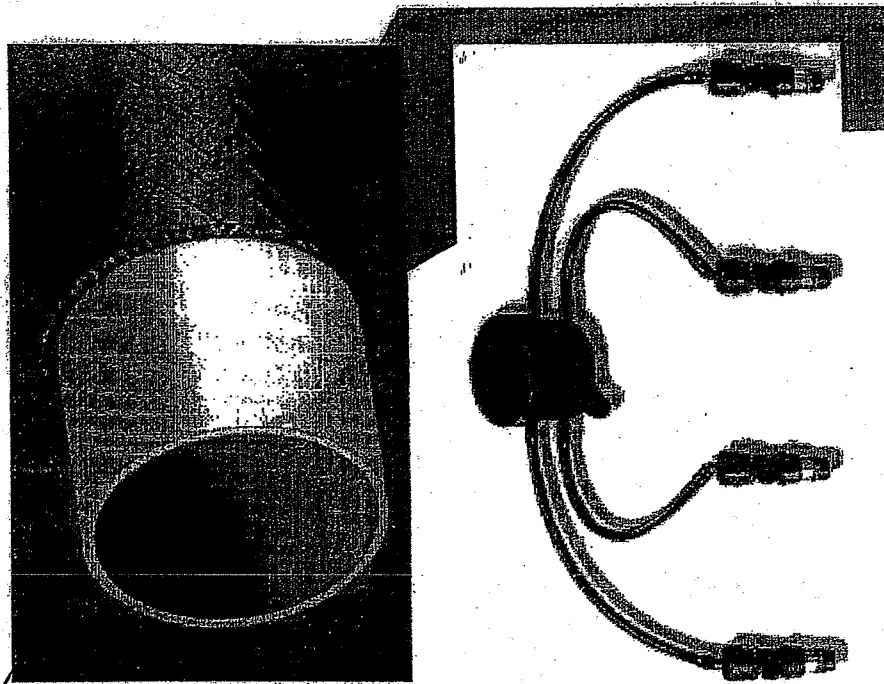
Societal Benefits: Passenger protection; aircraft reliability
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Automotive/Transportation



Key requirements: Chemical and temperature resistance; electrical performance; lubricity

Major uses:

- Seals, bushings
- Fuel and brake hoses/tubing
- Control cables
- Underhood wire

Societal Benefits: Lower vehicle weight and emissions; reliability

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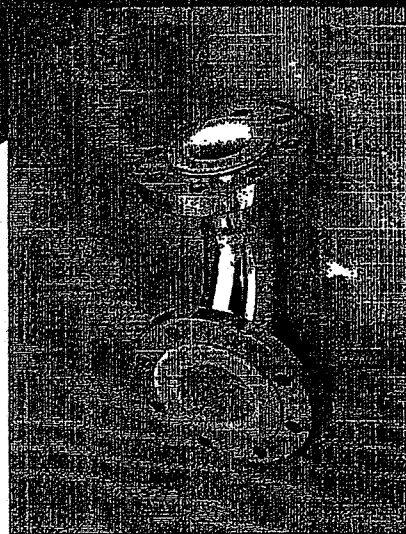
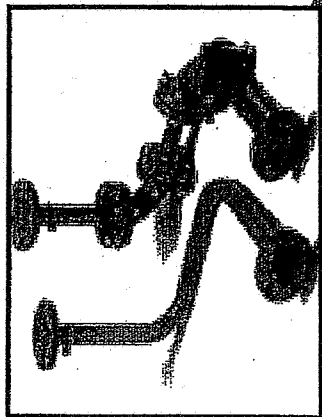
Chemicals/Petrochemicals

Key requirements: Chemical and applications temperature resistance; non-stick

Major uses:

- Lined pipes, valves, pumps
- Tank and reactor linings
- Gaskets, seals
- Wire insulation

Societal benefits: Worker and public safety; industry productivity
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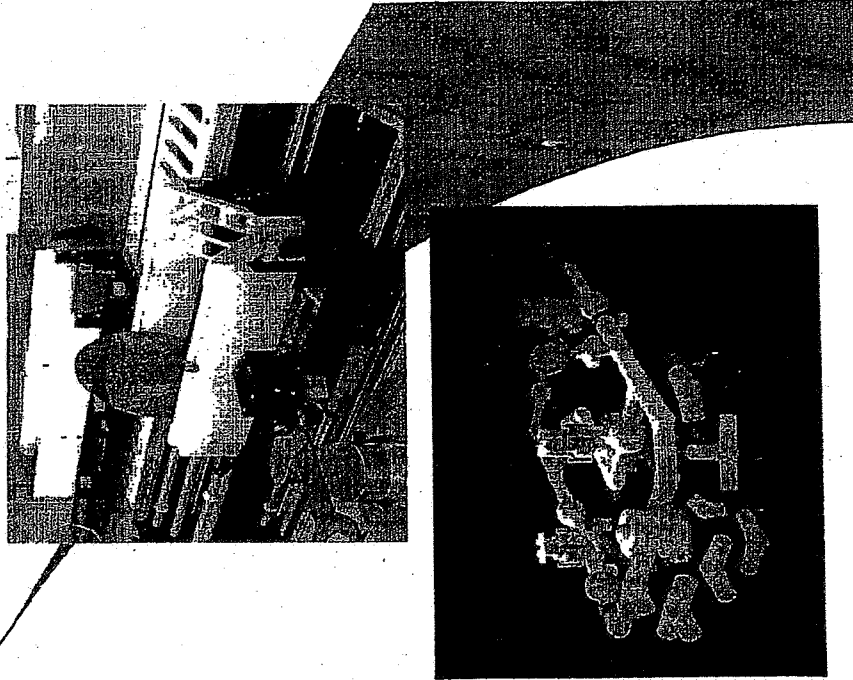


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Semiconductor/Electronics



Key requirements: Chemical and temperature resistance; purity; electrical performance

Major uses:

- High-purity fluid handling equipment
- Silicon wafer carriers
- Clean room garments

Societal benefits: Consumer product quality and cost; industry productivity

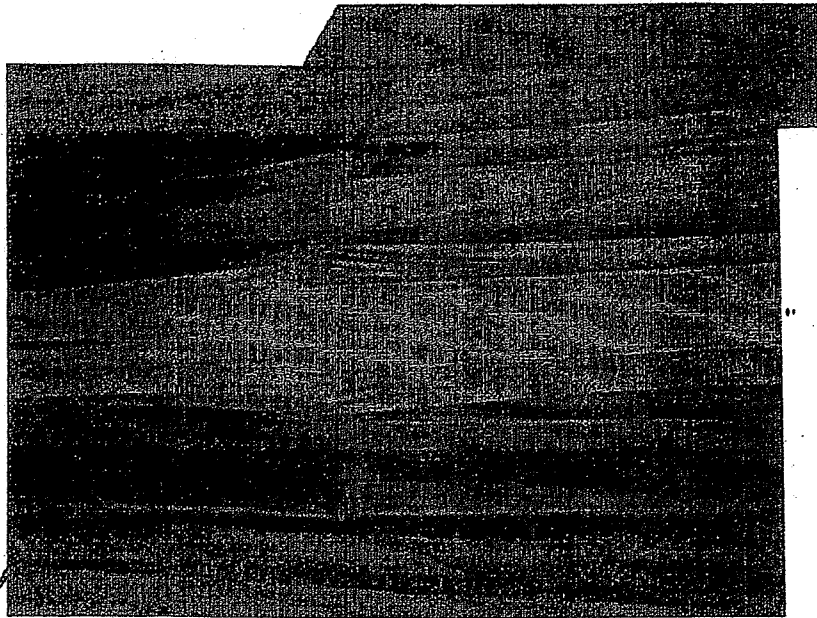
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Power Generation/ Pollution Control



Key requirements: Chemical and temperature resistance; flexibility

Major uses:

- Acid resistant filter bags
- Radiation resistant wire insulation
- Expansion joints

Societal benefits: Fewer emissions to the environment; worker and public safety; process reliability

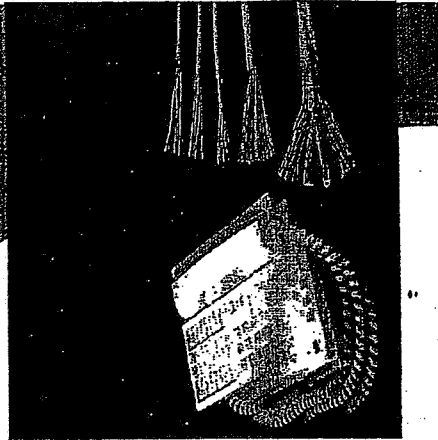
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Telecommunications



Key requirements: Electrical performance; fire resistance; optical properties

Major uses:

- LAN Cable
- Mainframe wiring
- Satellite wiring
- Fiber optic cladding and cable

Societal benefits: Public safety; critical systems reliability
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Consumer Housewares/Apparel

Key requirements: Non-stick; temperature resistance; easy to clean; hydrophobic

Major uses:

- Non-stick cookware and bakeware
- Waterproof/breathable clothing
- Appliance wiring

Societal benefits: Enables low-fat cooking; supports healthy lifestyle; consumer convenience

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Fluoropolymer Applications

Summary

- Fluoropolymers provide unique and critical performance properties in "system critical" applications that protect and benefit people and the environment.
- For virtually all applications, fluoropolymers are the only materials that meet system performance needs.
- Application design and best-available technology based on fluoropolymers.

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Fluoropolymer Applications

Summary (contd.)

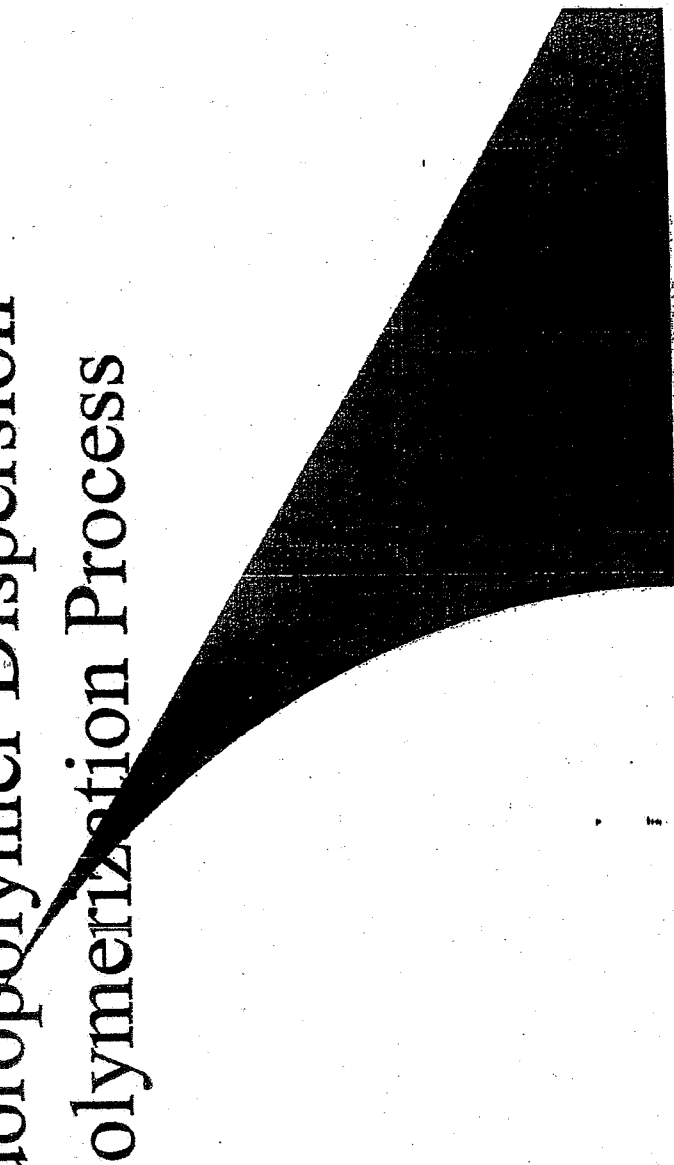
- Original Equipment technology and investment based on fluoropolymers
- Not-in-kind technologies for some applications have negative environmental impact and/or are cost prohibitive.

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Importance of C-8 in Fluoropolymer Dispersion Polymerization Process



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DISPERSION POLYMERIZATION PROCESS

INGREDIENTS

- Monomer(s) with extremely high purity
- Water (demineralized)
- Initiator (an oxidizing agent with high purity)
- Surfactant (non-telogenic, high purity)
- Optional other ingredients

EQUIPMENT

- Gently stirred heated reactor

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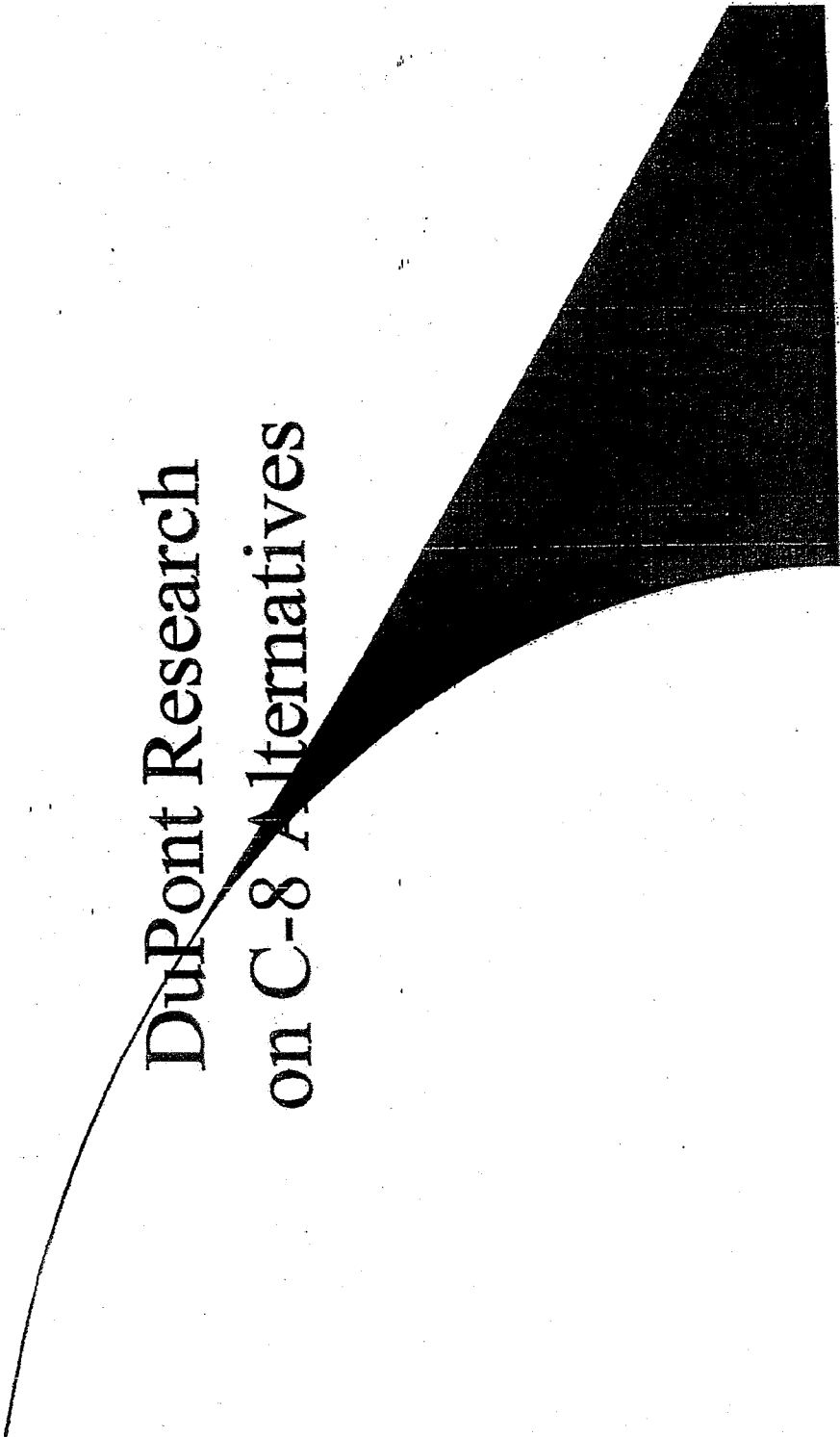
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CRITICAL AQUEOUS POLYMERIZATION FACTORS

- Facilitates:
 - Efficient heat removal
 - Particle architecture and/or size
 - Molecular weight and its distribution
 - Comonomer content and its distribution
 - High to extremely high molecular weight

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DuPont Research on C-8 Alternatives

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Efforts to Replace C-8

- 30+ Year Effort
- Millions of Dollars Invested in Research
- More than 40 Compounds Identified and Evaluated

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PHASES OF SURFACTANT EVALUATION

Surfactant

- ✓ Design and synthesis.
- ✓ Prepare candidates in a quantity large enough for research and development evaluation.
- ✓ Get samples of suitable surfactants from non-DuPont sources.

Polymerization

- △ Experiment with variety of product lines where the candidate surfactant may be suitable.
- △ Evaluate processing performance in post-reactor steps.
- △ Characterize products and compare the properties and application performance with standard products.

Health and Environmental

- Toxicological/persistence testing at Haskell Lab.

Total Assessment

After gathering all of the above, assess if a large scale test is appropriate.

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Requirements For A C-8 Alternative

- Low Persistence, Bioaccumulation and Toxicity
- Allows High-Quality Polymer Manufacturing
- Does Not Affect Performance In Use

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POTENTIAL SURFACTANT CANDIDATES EVALUATED

(1971-1999)

$\text{CHF}_2(\text{CF}_2)_7\text{CO}_2\text{NH}_4^+$ (Poly)
 $\text{CF}_3(\text{CF}_2)_8\text{CO}_2\text{NH}_4^+$ (Poly)
 $\text{CF}_3(\text{CF}_2)_7\text{CO}_2\text{NH}_4^+$ (Tox)
 $\text{CF}_3(\text{CF}_2)_3\text{CH}_2(\text{CF}_2)_2\text{CO}_2\text{NH}_4^+$ (Tox)
 $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CF}_2\text{CO}_2\text{NH}_4^+$ (Tox)
 $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{CF}_2\text{CO}_2\text{NH}_4^+$ (Poly)
 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{CF}_2\text{CO}_2\text{NH}_4^+$ (Tox)
 $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{CF}(\text{CF}_3)\text{CO}_2\text{NH}_4^+$ (Tox)
 $\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_3\text{CF}_2\text{CO}_2\text{K}^+$ (Poly)
 $\text{C}_8\text{F}_{17}\text{CO}_2\text{NH}_4^+$ (Branched) 3M confidential (Poly)
 $\text{C}_9\text{F}_{19}\text{CO}_2\text{NH}_4^+$ (Branched) 3M confidential (Poly)
 $\text{C}_{10}\text{F}_{21}\text{CO}_2\text{NH}_4^+$ (Branched) 3M confidential (Poly)

$\text{F}(\text{CF}_2)_n(\text{CH}_2)_2\text{OSO}_3\text{M}^+$ (Poly)
 M= Li, Na, Li, NH₄ (Poly)
 $\text{F}(\text{CF}_2)_6(\text{CH}_2)_2\text{SO}_3\text{H}$ (Poly)
 $\text{F}(\text{CF}_2)_6(\text{CH}_2)_4\text{SO}_3\text{H}$ (Poly)
 $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{SO}_3\text{Na}^+$ (PT)
 Ph= phenyl
 $\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{K}^+$ (Poly)
 $\text{F}(\text{CF}_2)_n(\text{CH}_2)_2\text{OSO}_3\text{M}^+$ (Poly)
 M= Li, NH₄
 $\text{H}(\text{CF}_2)_{10}\text{CH}_2\text{OSO}_3\text{NH}_4^+$ (Poly)
 $\text{F}(\text{CF}_2)_7\text{CH}_2\text{OSO}_3\text{NH}_4^+$ (Poly)
 $\text{NH}_4\text{O}_2\text{C}[\text{CF}(\text{CF}_3)\text{OCF}_2]_2\text{CF}_2\text{SO}_2\text{NH}_2$ (Poly)

Tox - Toxicity (acute or sub-acute),
 Persistence
 Poly - Deficiency in polymerization
 PT - Deficiency in post-treatment

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POTENTIAL SURFACTANT CANDIDATES EVALUATED (contd.)

(1971-1999)

$C_9F_{17}OPhSO_3^-Na^+$ Ph = phenyl (PT)
 $C_9F_{17}OPhSO_3^-NH_4^+$ Ph = phenyl (PT)
 $C_6F_{11}OPhSO_3^-Na^+$ Ph = phenyl (PT)
 $CF_3(CF_2)_2O[CF(CF_3)CF_2O]_2CF(CF_3)CO_2^-NH_4^+$ (Tox)
 $CF_3O(CF_2O)_3CF_2CO_2^-NH_4^+$ (Poly)
 $CF_3O(CF_2O)_5CF_2CO_2^-NH_4^+$ (Tox)
 $CF_3CH_2OCF_2CHFCF_2CF(CF_3)OCF_2CO_2^-NH_4^+$ (Tox)
 $CF_2ClCFClOCF_2CF(CF_3)OCF_2CO_2^-NH_4^+$ (Poly)
 $CF_3(CF_2)_5SCH_2CO_2^-NH_4^+$ (Poly)
 $CF_3(CF_2)_5CH_2CO_2^-NH_4^+$ (Poly)
 $CF_3(CF_2)_5CH_2CO_2^-K^+$ (Poly)
 $CF_3(CF_2)_7CH_2CO_2^-NH_4^+$ (Poly)

$CF_3(CF_2)_5CH_2CH_2CO_2^-NH_4^+$ (Poly)
 $CF_3(CF_2)_4COOH$ (Poly)
 $CF_3(CF_2)_7SO_2^-NH_4^+$
 $CF_3(CF_2)_7SO_2^-Na^+$ (Poly)
 $CF_3(CF_2)_5SO_2^-NH_4^+$ (Poly)
 $CF_3(CF_2)_3SO_2^-NH_4^+$ (Poly)
 $CF_3(CF_2)_3SO_2^-NH_4^+$ (Poly)
 $CF_5(CF_2)_6CN_4^-NH_4^+$ (Poly)
 $CF_3(CF_2)_5CH_2CH_2CH_2N(CH_3)_3^+Cl^-$
 $CF_3(CF_2)_6CH_2OPO_3^- = (NH_4^+)_2$ (Poly)
 $CF_3(CF_2)_nCH_2CH_2OPO_3^- = (NH_4^+)_2$ (Poly)

Tox - Toxicity (acute or sub-acute),
persistence

Poly - Deficiency in polymerization
PT - Deficiency in post-treatment

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Technical Summary

- Fluoropolymers can be made into useful parts only when they have high molecular weight. For some applications, extremely high molecular weight is critical.
- The majority of DuPont's products are dispersion polymers and require very pure ingredients, including the surfactant, to have high molecular weight.
- Impurities containing hydrogen cause a significant reduction in molecular weight.
- All of the above create a limit in the choice of surfactant. C-8 is currently the only suitable surfactant for most fluoropolymers, and is used by DuPont and other manufacturers worldwide.
- Over the last 30 years, DuPont has invested substantial resources to find an alternative to C-8 but has been unsuccessful.

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Industry Initiatives Concerning C-8

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Industry Groups

- Association of Plastics Manufacturers Europe (APME)
- Society of Plastics Industry - Fluoropolymer Manufacturing Group (SPI-FMG)

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Industry Group Activities

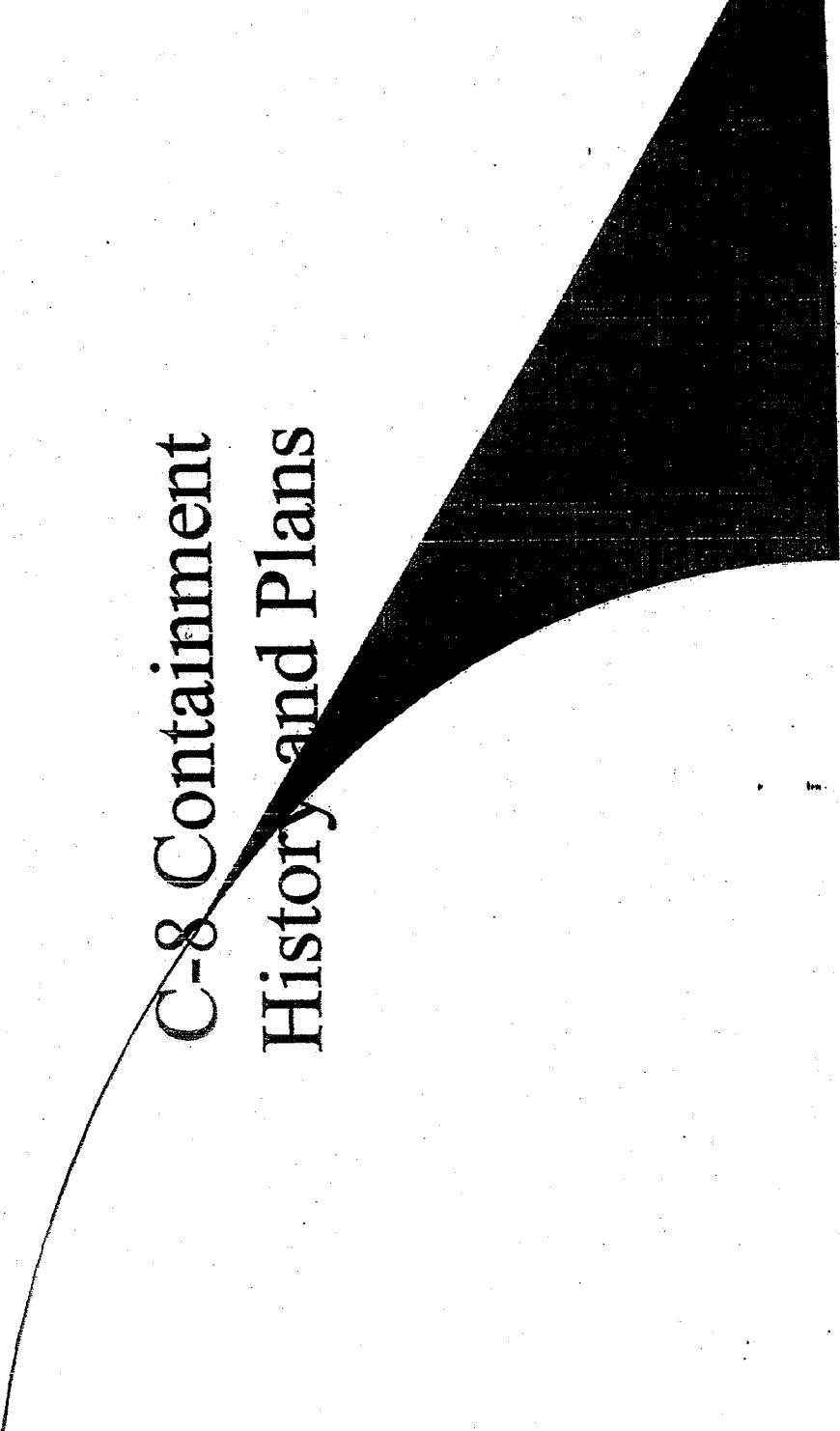
- Global Material Balance
- Toxicity and Environmental Testing
- Voluntary Commitment to Contain
- DuPont Technology Sharing
 - Capture for Destruction - license free
 - Capture for Recycle
- Alternatives Discussion

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C-8 Containment History and Plans



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C-8 History at Washington Works

- 1950s: Surfactants used for PTFE polymerization, C-8 selected as surfactant for DuPont PTFE production.
- 1970s: C-8 use expanded to co-polymer and fluoroelastomer production. Alternatives first investigated.
- Late 1970s: C-8 persistence first recognized in worker. Began programs to reduce worker exposure.
- 1982: Began R&D to reduce emissions
- 1989: DuPont installs first C-8-specific scrubber.

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Elements of C-8 Stewardship 1990 to Present

- Reduce Releases
- Reduce Use
- Recycle
- Destroy
- Evaluate Alternatives

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Current C-8 Emission Reduction Programs

- All major emission points have control device installed.
- Efficiency varies from >90% to about 50% due to technological difficulties.
- Additional programs identified to take total site emissions to <5 tonnes/yr.

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Current Reduction/Recovery Projects

<u>Program</u>	<u>Year to be implemented</u>
● Upgrade water Removal Facility	Complete
● Capture/Destroy C-8 In Supernate Waste	2002
● Improve Efficiency of Copolymer scrubbers	2002
● Capture Particulate from Fine Powder Scrubber	2002
● Increase C-8 Recovery Facility Efficiency	2002
● Alter Emission point Design	2002
● Recover C-8 from Wastewaters	2004

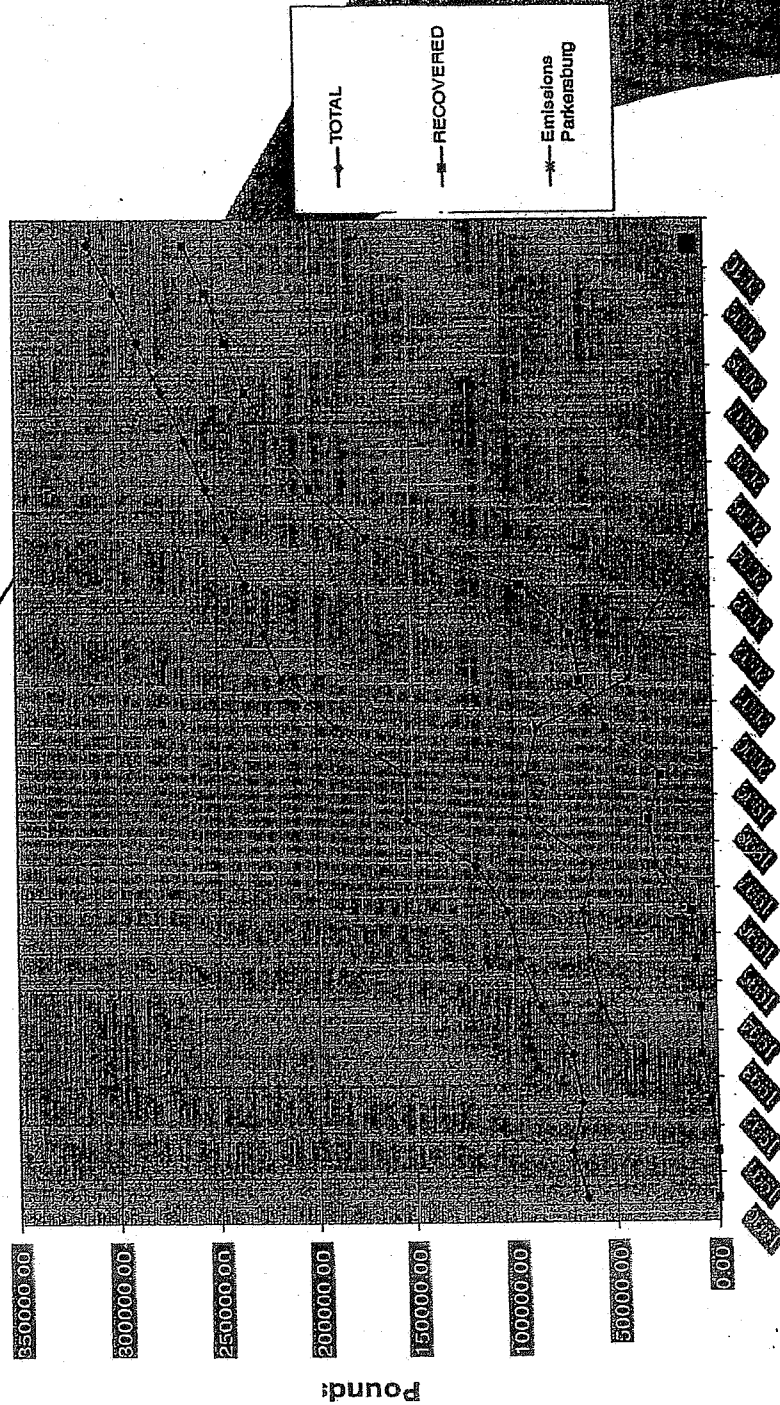
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**C-8 Use, Recovery and Emissions in Washington Works Area
1990 through 2010**



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Summary of Efforts to Reduce Emissions and Exposure

- DuPont has been working on C-8 emission reduction for 20+ years.
- More than \$15 million invested since 1988; another \$15 million planned by 2003.
- 75% of C-8 recovered or destroyed in 2001; will be 90% by 2004. Rest of industry capturing little or none.
- DuPont making recovery/recycle technology available to competitors.
- Working with EPA and other agencies to increase knowledge C-8.

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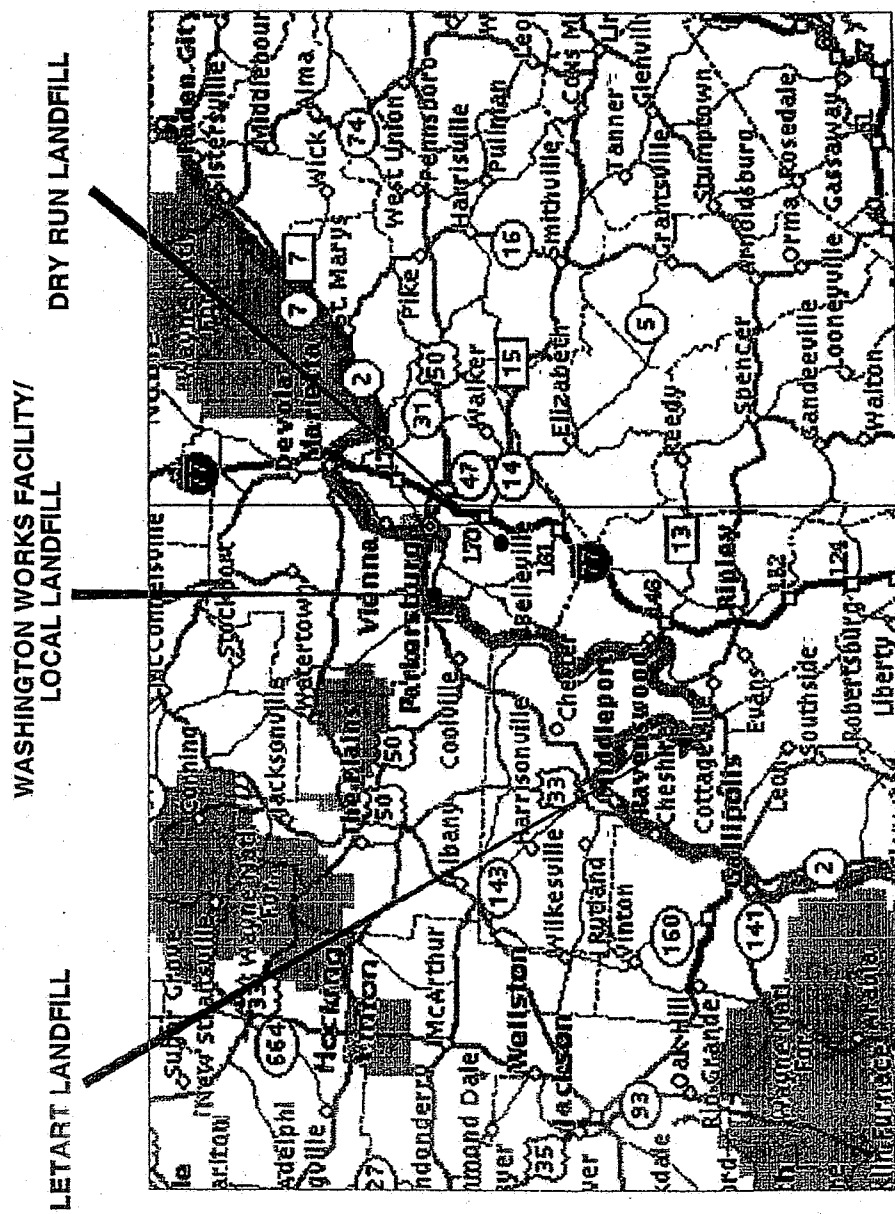
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Presence of C-8 in
Little Hocking, Ohio

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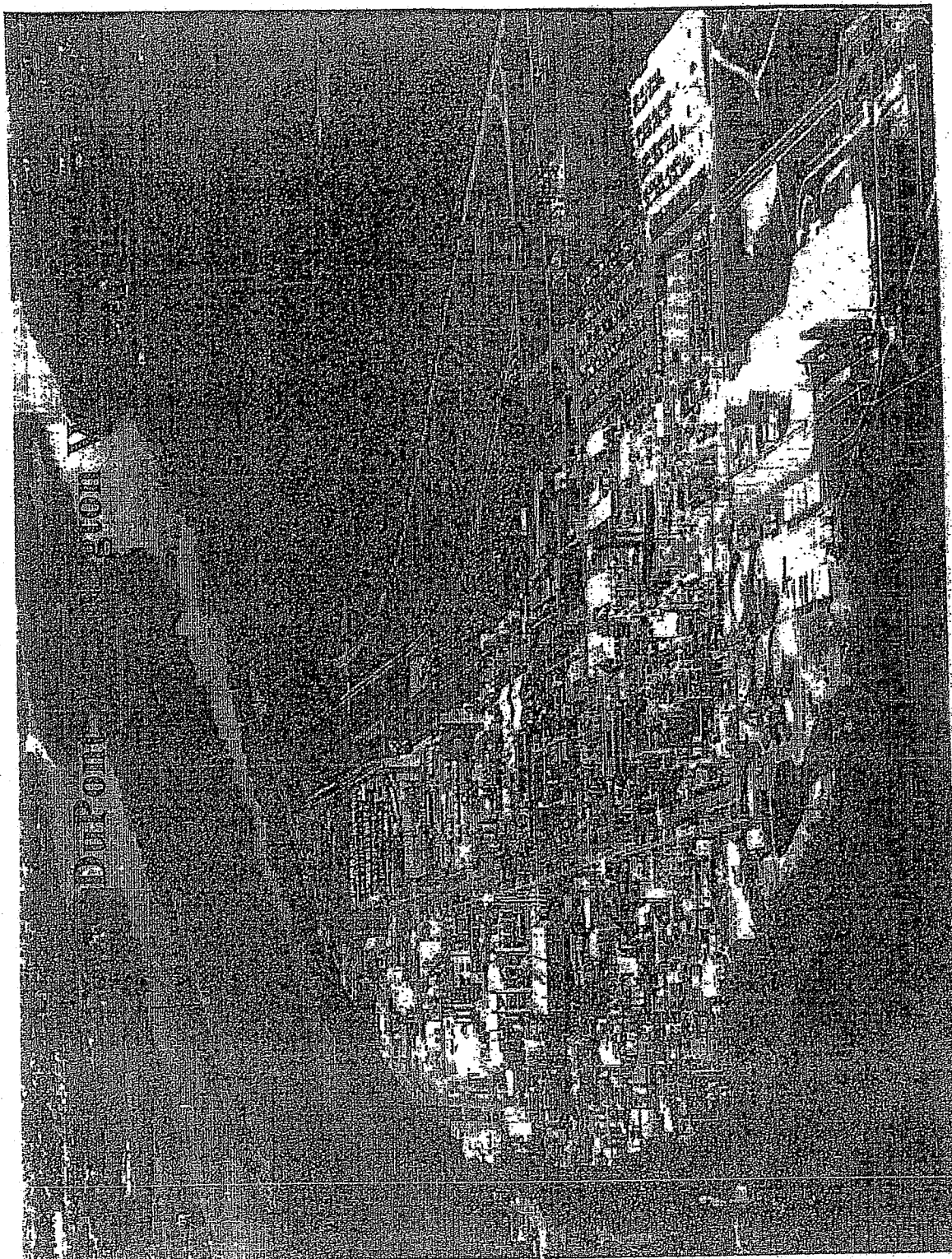


DUPONT WASHINGTON WORKS PROPERTIES

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Potential Sources of C-8 in Little Hocking Public Water Systems

- Groundwater migration from Washington Works site.
 - Updating groundwater model to include information provided by the LHPWS.
 - Will be sampling groundwater in LHPWS monitoring wells to discern direction of source.
- Air deposition from plant emissions migrating to groundwater.
 - Ambient Air and deposition modeling (EPA models) complete
 - Will combine deposition with modeling of transport from surface to groundwater (using established EPA protocols for crop protection chemical studies).
 - Will compare results to measurements to determine if deposition is significant contributor.

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Multi-Media Consent Order

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Consent Order Purpose

"To determine whether there has been any impact on human health or the environment as a result of releases of C-8 to the environment from DuPont operations."

- Entered into with WVDEP and WVDHHR
- Effective Nov 15, 2001

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Consent Order Requirement #1

A. Establish a Groundwater Investigation Steering Team (GIST)

- Purpose: Assess presence and extent of C8 in drinking water, groundwater, surface water at and around WW and landfills
- WVDEP, WVDHHR, EPA Region III, DuPont
- Funded by DuPont
- Report findings and conclusions regarding groundwater
- Report recommendations regarding further work or action

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Key Tasks of the GIST

- Groundwater use and well survey
- Identify and sample all groundwater wells within 1 mi. radius of WW and landfills, with provisions to expand sampling range based upon results
- Assess groundwater and surface water monitoring data and develop a groundwater monitoring plan and schedule
- Determine the extent of any C8 impacted groundwater

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Requirement #2

B. NPDES Sampling

- Monthly sampling for C8 at Landfills and at outfalls 1, 2, 3, 5, 7, and 105
- Sample each surface or alluvial water intake for public water supplies along Ohio River for 1 mi. upstream and 1 mi. downstream
- if detected, successive expansion of sampling range

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Requirement #3

C. Establish a "C-8 Assessment of Toxicity Team" (CAT Team)

- Purpose: Assess the toxicity and risk to human health and the environment associated with exposure to C-8 released from DuPont activities
- WVDEP, WVDHHR, EPA Region III, NICS, ATSDR
- Funded by DuPont
- Report findings and conclusions as to what extent there may be of health risk associated with C-8 at the facilities

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Key Tasks of the CAT Team

- Hold Public Meeting to introduce the parties, relate historical C8 levels in LPSD water, relate ensuing activities, and invite participation in sampling and survey efforts (Domestic, 29/01)
- Review available toxicology and epidemiological data
- Develop Screening Levels for protecting human health
- Conduct a risk assessment comparing exposures to Screening Levels
- Second Public Meeting to present results of GIST and CAT Team efforts, air modeling results, and any further actions

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Requirement #4

D. Air Emissions Modeling Assessment

• Provide information to WVDEP DAQ to facilitate, including:

- building dimensions
- allowable and actual emission rates
- stack parameters
- physical property data
- particle characterization
- scavenging coefficients

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Requirement #5

E. C-8 Reduction Program

1. Limit overall C8 emissions to air to year 2000 levels
 - report emissions monthly, transitioning to quarterly upon issuance of Screening Level
2. Reduce emissions to air and discharges to water column by 50% from actual 1999 levels by year-end 2003
3. Operate and maintain filter and carbon bed system with 90-95% C8 removal efficiency in major C8-containing wastewater stream
4. Install improved scrubber filter in Fluoropolymer area
5. Conduct scrubber optimization and recovery improvement program and implement if encouraging

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Requirement #6

F. In event of demonstration of C8 exposures above the Screening Levels developed per this Consent Order, submit a plan for reducing such exposures below the Screening Levels in a reasonable time

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