

Montreal Protocol



Process Agents Task Force

Case Study #10

Use of CFC 11 in manufacturing a fine synthetic fiber sheet structure

May 2001

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CS-10 Use of CFC 11 in manufacturing a fine synthetic fiber sheet structure

CS-10.1 Introduction of process

CS-10.1.1 Products made, use of the products:

Fine synthetic fibers are formed into strong sheet structures used for a variety of important applications including:

- Air infiltration barriers in buildings to reduce heating and air conditioning costs and to extend the useful economic life of wooden building material (by excluding water rot)
- Medical device packaging that allows sterilization after packaging and providing long, safe, shelf life
- Protective clothing for workers handling toxic or dangerous chemicals (i.e. asbestos removal)
- Packaging for important products and information in tear resistant light-weight envelopes that save shipping costs and assure intact long distance delivery
- graphic applications that ensure long life of maps, banners, tags, under severe climate or service conditions
- special purpose clothing, packaging, padding, and insulating applications

CS-10.2 Description of overall manufacturing process:

Fine synthetic polyolefin fibers are manufactured using CFC-11 as a process agent. CFC-11 is contacted with high density polyethylene pellets in a slurry mix tank, pumped with high pressure pumps through a heat exchanger and stirred tank mixers to form a spinnable polymer solution.

Using a manifold, the polymer solution is fed to spin packs. Filaments are spun into a spin cell and onto a belt to form a sheet structure which is consolidated, extracted from the spin cell through seals rolls, devolatilized inside an air enclosure before being wound-up. The process agent, in vapor form inside the spin cell, is entirely recovered, neutralized and returned to storage.

CS-10.3 Why is the ODS used as process agent ?

QUALITY OF FINAL PRODUCT	PURPOSE XX
SAFETY NECESSARY FOR CHEM. REACTION	X
YIELD	X
COST	X
OTHER	

Notes to Table: X signifies the main purpose, XX signifies a secondary purpose

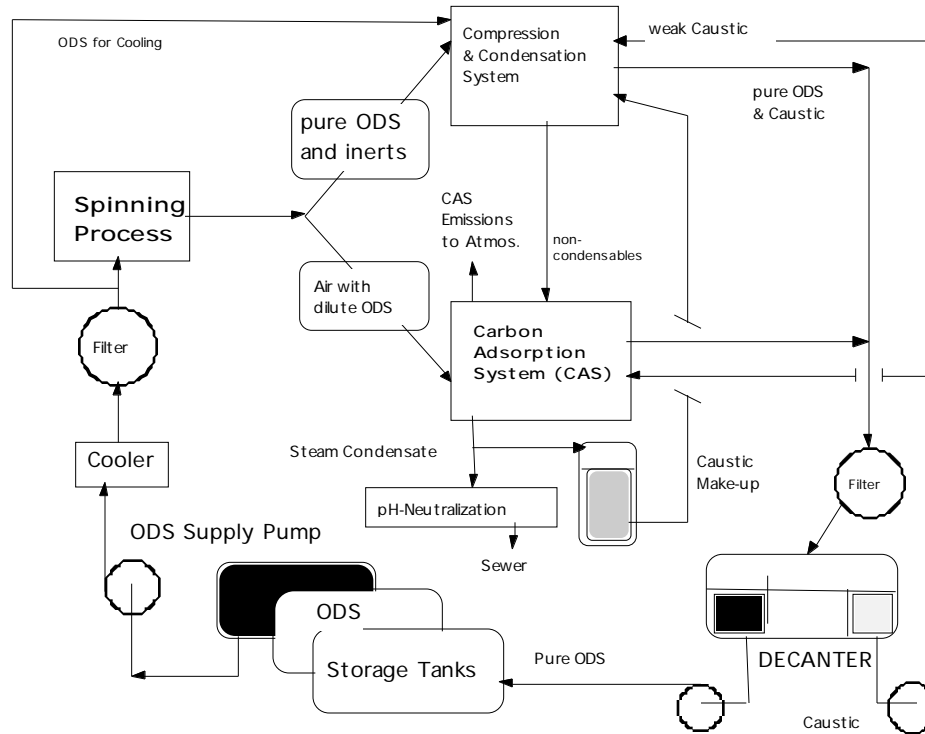
CS-10.3.1 Unique process agent properties:

- low toxicity
- non flammable
- physico-chemical properties: boiling point,
- critical temp. / pressure
- solvency power (capability to enter polymer matrix)
- controls solution viscosity and process operating pressures
- chemical stability to high temperature and pressure
- non corrosive

CS-10.4 How the ODS is used as process agent

Fine Synthetic Fiber Sheet Structure: Process Agent Recovery Flow

C.Metzdorf 10/96



CS-10.4.1 Efficiency of ODS recovery after use

Typical ODS recovery efficiencies are 99.96 - 99.99 %, recognizing a circulation of 19-24 tons/h in each production line.

CS-10.4.2 Disposal of the ODS

The goal of the ODS containment process is the total recovery within the direct manufacturing boundaries. Disposal is not applicable to the type of ODS used. The recovery process has a blowdown collection tank able to collect 'contaminated' ODS from the process and boil-off the pure ODS to be recovered.

CS-10.4.3 Quantity required for make-up, past and future changes

Total process agent make-up quantity is in the 50 to 75 tonnes per year range reflecting different equipment utilization rates.

CS-10.4.4 Process Agent Losses: past and future changes for total global capacity:

Year	Locations/Lines	Losses [Tonnes]	Losses as % of '86 base
1986	U.S./2	2323	100
1987	U.S./2	1626	70
1988	U.S./2	1211	52
1989	U.S./EU/3	813	35
1995	U.S./EU/3	131	< 6
2000	U.S.	52	<2.3

It must be noted that approx. 10 % of the process agent losses are the result of ODS transformation or destruction, not from a diffuse or point source emission. In fact chloride salts measured in the active carbon adsorption system steam condensate neutralization station confirm the ODS transformation and destruction mechanism.

CS-10.5 Pollution abatement

General description of control technology. The CFC-11 Recovery process essentially distinguishes between:

CS-10.5.1 Primary Recovery (CCS)

The main process agent flow (approx. 24,000 kg/h) from the spincell (volume 1000 m³) is recovered in a 'compression and condensation system' (CCS) utilizing a spraycooler, compressor, condenser and vent condenser. Recovered liquid is neutralized with caustic water injection, decanted before being pumped back to storage. Non-condensables vent to CAS.

CS-10.5.2 Carbon Adsorption System (CAS)

Process agent vapors from the sheet devolatilization process inside the air enclosure and other small quantities or dilute sources of process agent from process equipments are conveyed to the Carbon Adsorption System. Roughly 3 % of the main process agent flow is recovered in CAS.

Steam condensate from CAS containing trace amounts of process agent is recovered using a steam stripper. The Carbon Adsorption System presents a 'point' emission source.

Recovery Systems in place during upset conditions:

Following devices recover the process agent during process upset conditions:

a) all vessels presenting a vapor space with potential vapor pressure build-up are protected with a rupture disc connected to a containment tank. In case of spincell overpressurization due to recovery compressor failure, process agent vapors are also collected in this containment tank. Recovery of containment tank vapors takes place via CCS and CAS.

b) cold liquid process agent from rupture disk discharge lines are collected in a collection tank. Cold pellet/process agent slurry rupture disk discharge lines first pass a pellet collection tank before the liquid process agent is recovered in the blowdown collection tank.

c) hot process agent and polymer solution rupture disk discharge lines are connected to a flash tank. Flashing of polymer solution in the flash tank produces a fluffy polymer material that requires separation by time and temperature. These vapors are returned to the CAS for recovery.

Diffuse emissions from valves, gaskets, etc. inside the building, including the pack change sequence which involves the opening of the spincell to exchange a spin position, are reported as fugitive emissions.

CS-10.5.3.a Recovery System Design Considerations:

Measures to collect routine losses previously not controlled:

- enclosure of sheet handling section of spinning machine
- tightening of spin cell windows, new gaskets and local CAS vapor evacuation capability in case window has to be opened to remove polymer from inside machine spinning packs to maintain continuity
- additional partition wall in secondary enclosure to avoid dilution and provide second counter current air stripping slot
- installation of containment tanks to capture ODS from over-pressurization of spin cell and blowdown cell
- Venting of spin deck pack change 'bathtub' arrangement and pack cavity to Carbon Adsorption System (CAS)
- CAS air capacity increased to capture more air from different area enclosures and ODS supply system

- impulse lines reduced to minimum essential length to avoid fittings at elbows which eventually leak due to associated equipment vibrations
- additional headers with connections to CAS to all areas requiring maintenance work and quick containment of small leaks
- more frequent and extensive inspection, preventive maintenance and system upgrades
- Carbon Adsorption System Upgrade:
- CAS Steam-out manifold modified to avoid carbon blow-out and steam channeling
- high temperature steam supply for CAS steam-out; HP/LP steam ratio allows higher steam-out pressure to desorb more ODS
- CAS air capacity increased to capture more air from different areas
- spare and backup equipment installed

1995/1996

- close monitoring of all CAS valves (corrosion of valves has impaired proper functionality)
- exchange of active carbon after 3-7 years of service (9 tons of active carbon per bed)
- Control of Losses with Steam Condensate Discharge to Sewer:
- CAS condensate is steam stripped before discharge
- CAS and Compression & Condensation System (CCS) combined to minimize caustic turn-around and ODS lost with aqueous discharge
- Steam Condensate multi-stage steam stripping prior to discharge to plant process sewer
- CAS steam condensate/caustic flows redesigned to scale-down discharge to plant process sewer

- water skimming equipment installed in all five ODS storage tanks for removal of decanted water (water being entrained into the tanks from the caustic neutralization process during recovery)

Pressure Relief Containment:

ODS / Slurry System

- process pressure rating designed to control slurry pump rather than have polymer/ODS release to atmosphere
- containment and auto shutdown of slurry pump in the event of cold slurry rupture disc failure
- additional protection of all relief valves with rupture discs
- all cold/slurry relief lines connect to a pellet collection tank tied to the collection tank for evaporation of the cold ODS

ODS Vapor

Concept: Containment Tanks

- all vessels presenting a vapor space with potential vapor pressure build-up are protected with a rupture disc connected to - various containment tanks..
- both the spin cell and the blowdown tank are connected to a - containment tank. In case of spin cell over-pressurization due to recovery equipment (compressor) failure, process agent vapors are also collected in this containment tank.
- Recovery of containment tank vapors takes place via CCS and CAS.
- the spin cell containment tank has capacity for 10 minutes of major equipment failure prior to procedural shutdown of the process once the tank level alarms at 75 %
- Polymer Solution and Flush System
- all (17) rupture discs located in the high pressure polymer solution or flush system are connected to a flash tank. Flashing of polymer solution in the flash tank produces a fluffy polymer material that requires separation - before the process agent vapors are collected.

CS-10.53.b Process Control Strategies: Monitoring

CS-10.5.3.b.1 Maximize Process Control

Redundant Distributed Control System (DCS)

- > 300 control loops
- >5000 monitored data points
- Flexible multivariable central control functions
- Computer assisted Carbon Adsorption System Troubleshooting
- Process Equipment: Spare and Protection
- Spare ODS Compressor.
- Spare Carbon Adsorption System Blower
- Design done with Power-dip consideration allowing ride-through in case of minor interruption (< 0.7 sec.) and safely shutdown with contained ODS situation in case of major power loss

Miss-operation and Equipment Failure Protection:

- Power dip ride-through ability up to 15 seconds with main drives of process, automatic shutdown of spinning and solutioning systems in the event of a major power dip in order to maximize ODS containment
- On-line spare ODS compressor available, remote S/U from DCS
- On-line spare CAS blower
- Automated DCS control of spin cell charging with ODS to control losses from recovery system upsets and over-pressurization of spin cell.
- ODS flushed from Solutioning process and solution filters via additional heat exchanger to Blowdown Cell: ODS is superheated to eliminate liquid accumulation in Blowdown Cell
- Blowdown Cell walls heated to prevent condensation during Start-up and ODS accumulation in polymer mass after shutdown

Focus on Human Control Aspect

Provide adequate Control Tools

- air monitoring sample points have been quadrupled to 80 points - for quick detection of local losses
- IR analyzers for spot measurements and trace analysis have been doubled to a total of 6
- Gas chromatographic analysis and alarm system for plant exhaust air
- Major project authorized to upgrade process and control equipment

CS-10.5.3.c The 'HUMAN' Factor

CS-10.5.3.c.1 Training and Failure Prevention

- Operator training; emphasis on process understanding and attention to detail
- Operators utilize all available tools (computerized troubleshooting, portable analyzers) to localize and contain area ODS leaks
- Operator Acceptance Test for process control responsibilities
- Total commitment to control losses from all plant personnel
- Leak incident reporting system with corrective actions
- Computer-based equipment to continuously monitor ODS inventories in tanks, piping systems, vessels, automatically providing alarms as well as day-to-day loss rates to operators and managers
- An operator suggestion system rewarding those suggestions implemented in the field
- Equipment lock-out procedure not only aimed at safety but also at environmental control
- During maintenance activities, ODS drained out of piping, vapors evacuated to CAS, and liquid collected in central drum before being pumped into central process "evaporator"
- Preventive Maintenance program to check mechanical integrity of all rotating equipment in contact with ODS

- Failure Mode and Effect Analysis (FMEA) performed for all routine practices, i.e. filter change, with the purpose of determining potential failures causes and work out procedures and or equipment modifications to avoid occurrence
- 'Zero Leak Team' Effort; cross section of organization analyzed all potential small leak sources and worked out solution to increase containment
- Strong analytical understanding of loss sources & material balances
- True technical team work with plant & Engineering. counterparts
- Multi-point analyzers for continuous building monitoring
- Wide spread attack with priority for large sources first
- Operator patrols to check for leaks (beyond automatic analyzers)

CS-10.5.3.d Public Opinion:

- Open relationship with local government officials via timely technical information meetings about containment status and programs
- Community Awareness and Emergency Response (CAER) as part of the 'Responsible Care' program to inform local communities of plant activities
- Plant visits by customers, government officials and interest groups are conducted to demonstrate efficient production & recovery facilities and discuss containment strategy

CS-9.5.4.2 Enforcement:

The plant management and employees are committed to strictly operate the facility according to local and/or international legislation.

CS-10.6 Substitutes without CFC-11

CS-10.6.1 Description

The fiber manufacturing area, including the solutioning, spinning and process agent recovery equipment, is the source of ODS losses.

No simple safe, drop-in process agent has been identified to replace CFC-11 in the existing production facilities. This is true despite an ongoing program (more than twelve years) that has examined over one hundred and twenty potential process agents. Scouting

work continues to search for a viable non-ODP spin agent that can be safely and effectively used in existing production facilities, but the probability of finding a successful process agent is considered to be low.

In a parallel effort, extensive R&D and pilot plant development work resulted in identifying a non-ODP process agent that is capable of producing fine synthetic fibers, but its physical, chemical and flammability characteristics require the construction of completely new, very expensive production facilities.

CS-10.6.2 Limitations

A pilot plant in the USA was authorized in January 1991, and was completed in May of 1992 to develop these new spinning processes. Significant learning's from the pilot plant have been incorporated in the-three new production facilities that have been built to date. These three facilities are in various stages of operation including: startup mode, facility rework and upgrading to relatively stable commercial operation.

- THE NEW PROCESS AGENT was one of the compounds in the original patents but, in the late 1960's, non-flammability made CFC's a better choice for development.
- The new process agent has unique process characteristics and the products produced with the new process agent have different properties that require significant product specification and process adjustments.
- This new spinning process includes about 70 % new technology, most of it being associated with the spin cell, spin pack hardware and for the commercial operation, the pack change technology used (and patented)
- The new production facilities and pilot plant continue to demonstrate new spinning hardware and procedures that are needed to safely manage the new process agent, combine it with the polymer, manage its recovery and recycling after spinning, de-volatilizing the sheet product and providing proper seals and ventilation.
- Pilot plant tests of a new safer mixing technology demonstrated acceptable process capabilities. This technical capability coupled with the belief that this mixing technology would provide a safer manufacturing process, resulted in selecting this new technology for the third new production facility. The new mixing technology has yielded positive process demonstrations in the third production line that began operation in IIQ 2000. This technical success has resulted in the decision to retrofit the first two production lines. This decision will result in significant production down time and very large additional capital expenditures.
- Process safety management is the key to maintain a safe operating environment.

- Because of the process and safety considerations identified above, all technical efforts are focused on finding and commercializing a more robust and inherently safer manufacturing process. Plans have been defined for a fourth generation production facility that should begin operation in 2002. It is expected that this fourth generation process will be the basis for additional production facilities in the future.