

Standard Operating Procedure and Checklist of Minimal Requisite Facilities for utilization of hazardous waste under Rule-9 of the Hazardous and Other Wastes (Management and Transboundary Movement) Rules – 2016

Utilization of Spent Sodium Sulphite {generated during caustic scrubbing of SO₂ from Pesticide, Dye & Dye intermediates, Pharmaceutical sector and, Organic Chemical sector during Chlorosulphonation reactions} in production of Sodium bisulphite for production process of dyes & dye intermediates, textile, and pulp & paper industries



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**Central Pollution Control Board
(Ministry of Environment, Forest & Climate Change,
Government of India)
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Utilization of spent sodium sulphite {generated during caustic scrubbing of SO₂ from Pesticide, Dye & Dye intermediates, Pharmaceutical sector and, Organic Chemical sector during Chlorosulphonation reactions in production process of dyes & dye intermediates, textile, and pulp & paper industries

Procedure for grant of authorization by State Pollution Control Board (SPCBs)/Pollution Control Committee (PCCs) for utilization of Hazardous waste

- 1) While granting authorization for utilization of hazardous wastes, SPCBs/PCCs shall ensure that authorization is given only to those wastes for which Standard Operating Procedures (SoPs) for utilisation have been circulated by CPCB ensuring the following:
 - a. The hazardous waste (intended for utilization) belongs to same source of generation as specified in SoP.
 - b. The utilization shall be same as described in SoP.
 - c. End-use/ product produced from the waste shall be same as specified in SoP.
 - d. Authorization shall be granted only after verification of details and minimum requisite facilities as given in SoP.
 - e. Issuance of passbooks (similar to passbooks issued for recycling of used oil, waste oil, non-ferrous scraps, etc.) for maintaining records of receipt of hazardous waste for utilization.
 - f. Monitor closely the quantity of Spent Sodium sulphite/ Spent Sodium bisulphite {generated during caustic scrubbing of SO₂ from Pesticide, Dyes & Dyes intermediates, Pharmaceutical sector and, Organic Chemical sector (chlorosulphonation reactions)} being sent by generators and the quantity being utilized by the authorized industries and the capacity of the utilizer industry in the State.
- 2) After issuance of authorization, SPCBs/PCCs shall verify the compliance of checklist and SoP on quarterly basis for initial 1 year; followed by random checks during subsequent period for atleast once a year. The compliance reports may be submitted to CPCB.
- 3) In-case of lack of requisite sampling and laboratory infrastructures with the SPCBs/PCCs, they may engage 3rd party institutions or laboratories having EPA/NABL/ISO17025 accreditation/recognition for monitoring and analysis of prescribed parameters in SoPs for verification purpose.
- 4) SPCBs/PCCs shall provide half yearly updated list of units permitted under Rule 9 of Hazardous & Other Wastes (Management & Transboundary Movement) [HOWM] Rules, 2016 to CPCB and also upload the same on SPCB/PCC website, periodically. Such updated list shall be sent to CPCB.
- 5) Authorization for utilisation shall not be given to the units located in the State/Union Territory where there is no Common TSDF, unless the unit ensures authorised captive disposal of the hazardous waste (if any generated during utilisation) or its complete utilisation or arrangement for transfer to authorised disposal facility.
- 6) In case of the utilization proposal is not same with respect to source of generation or utilization process or end-use as outlined in this SoP, the same may be referred to CPCB for clarification /conducting trial studies and developing SoPs thereof.
- 7) The source and work zone standards suggested in the SoP are based on E(P)A notified and OSHA/NAAQ standard, respectively. However, SPCBs/PCCs may impose more stringent standards based on the location or process specific conditions.

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- 8) SPCBs/PCCs shall ensure that the utiliser of Spent Sodium sulphite/ Spent Sodium bisulphite {generated during caustic scrubbing of SO₂ from Pesticide, Dye & Dye intermediates, Pharmaceutical sector and, Organic Chemical sector during Chlorosulphonation reactions} shall maintain daily records on National Hazardous Waste Tracking System (NHWTS).

109.0 Utilization of hazardous waste (H.W.):

Type of HW	Source of generation	Recovery/ Product
Spent Sodium Sulphite (Na ₂ SO ₃) (Category: 35.1 of Schedule-I under HOWM Rules, 2016)	Generated during caustic scrubbing of SO ₂ gas from Pesticide, Dye & Dye intermediates, Pharmaceutical sector and, Organic Chemical sector during Chlorosulphonation reactions	As raw material in the manufacturing of Sodium Bi Sulphite (NaHSO ₃) for ultimate usage in production process of dyes & dye intermediates, textile, and pulp & paper as reducing/bleaching agents

109.1 Source of Waste:

Spent Sodium Sulphite is generated during caustic scrubbing of SO₂ liberated in the Pesticide, Dyes & Dyes intermediates, Pharmaceutical sector and, Organic Chemical sector during Chlorosulphonation reactions* and it is categorized as hazardous waste under Category: 35.1 of Schedule-I under HOWM Rules, 2016 under HOWM Rules, 2016 which is required to be disposed in an authorized disposal facility in accordance with condition, when not utilized as resource recovery.

**Chlorination of Organic compounds using Sulphur Mono Chloride (S₂Cl₂), Thionyl Chloride (SOCl₂), and Sulfuryl chloride (SO₂Cl₂).*

Table 1. Typical Characteristics of Spent Sodium Sulphite

S.No.	Parameters	Spent Na ₂ SO ₃ from Pesticide sector	Spent Na ₂ SO ₃ from Organic chemical sector
1.	pH	10.7 - 12.5	9.7
2.	Purity	62 - 83%	12.17 %
3.	TOC	60 - 250 ppm	150 mg/L
4.	COD	-	416 mg/L
5.	Water/ Moisture Content	1.97%	79.23 %
6.	Chloride content	-	2.44 %
7.	Iron as Fe ₂ O ₃	0.0005 - 0.018%	0.02 %
8.	Lead	BDL	0.0003 %
9.	Mercury	BDL	ND
10.	Arsenic	BDL	ND
11.	Cadmium	BDL	0.00005 %
12.	Nickel	BDL	0.0002 %
13.	Sulphate as SO ₄	-	0.71 %

Note: SPCBs/PCCs to check the characteristics of Spent Sodium Sulphite prior to issuance of authorization, any significant deviation with respect to typical values mentioned in the table above may be examined with respect to the source or may be referred to CPCB.

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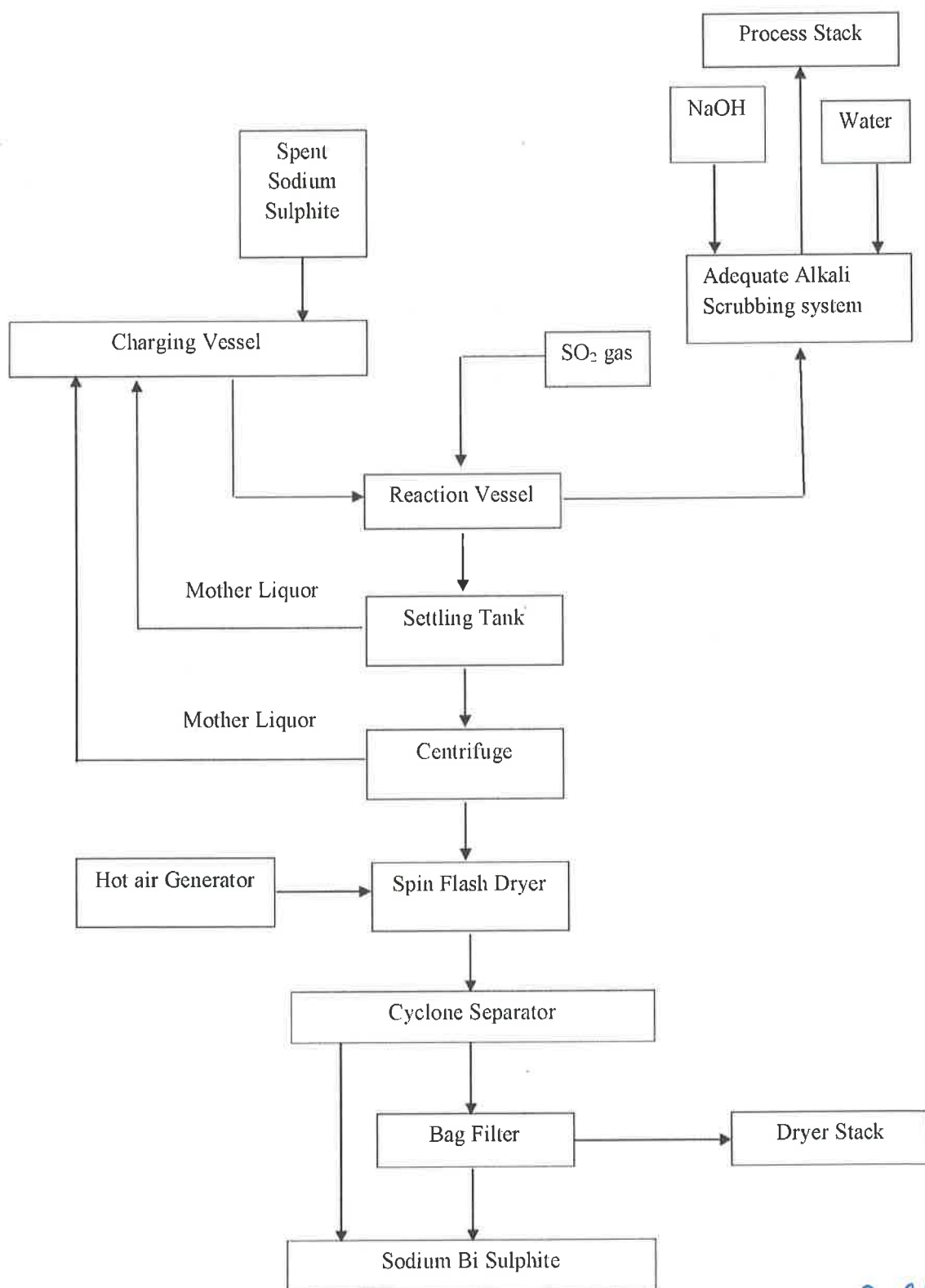


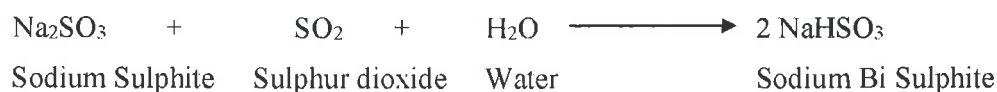
Figure: 1-Process flow diagram for utilization of Spent Sodium Sulphite

109.2 Utilization of Spent Sodium Sulphite at Production Stage:

Sulphur dioxide (SO₂) gas is purged into the mixture of Spent Sodium Sulphite and recycled Mother Liquor in the reaction vessel. The solution is transferred to the settling tank and the fumes generated in the reaction vessel are passed through an alkaline scrubber followed by stack.

In the settling tank, the solid material settles down while on the top is the mother liquor. The mother liquor is then sent to the charging vessel back, while the settled material is transferred to the centrifuge. The liquid extracted from centrifuge (mother liquor) is collected and transferred to the reaction vessel for next batch.

Centrifuged material is then transferred into Spin Flash Dryer. Hot air obtained from the hot air generator is passed with the centrifuged material to the Cyclone Separator followed by the Bag filter. Sodium Bi Sulphite (SBS) is collected from bottom of the cyclone separator and bag filter and the hot air released into the atmosphere from the stack attached to this system. The product is then collected and sent for the packaging.



109.3 Standard Operating Procedure for utilization of Spent Sodium Sulphite:

This SoP is applicable only for Utilization of Spent Sodium Sulphite {generated during caustic scrubbing of SO₂ from Pesticide, Dyes & Dyes intermediates, Pharmaceutical sector and, Organic Chemical sector during Chlorosulphonation reactions} in production of Sodium bisulphite for for ultimate usage in production process of dyes & dye intermediates, textile, and pulp & paper as reducing/ bleaching agents.

- 1) The utilizer (unit) shall procure solid Spent Sodium Sulphite in leakproof HDPE bags in trucks registered with SPCB/PCC fitted with requisite safeguards ensuring no spillage. In case of spent liquor of sodium sulphite, the material shall be transported in registered trucks/tankers/containers made of non-reactive material.
- 2) There shall be a designated space for unloading of Spent Sodium Sulphite into storage sheds. The receiving waste shall be placed above the ground and contained with low raise parapet/ bund wall with slope to collect spillages, if any.
- 3) The Spent Sodium Sulphite shall be stored in dedicated storage area (not in pits) on acid proof brick lined area under covered storage shed within premises with caution sign. Further, storage sheds shall have proper slope to collect seepage / floor washing.
- 4) The entire utilization process area shall have leak-proof and acid proof tiles with adequate slope to collect spillages, if any and shall be transferred to reaction tanks, as the case may be, through chemical process pump.



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- 5) The unloading, storage, transfer and other handling of hazardous waste (i.e., Spent Sodium Sulphite) shall be carried out using mechanical means avoiding manual intervention.
- 6) The spent sodium sulphite shall not have TOC levels >250mg/l.
- 7) The unit shall provide fume extraction system in the work zone and process area followed by APCD.
- 8) The reaction vessels shall be airtight to avoid any fugitive emissions. The reaction vessel shall be connected with common alkali scrubber of adequate capacity (connected with reactor). Adequate capacity may be achieved through the alkali scrubbers in series.
- 9) The dryer (such as spin flash dryer) provided shall be connected with cyclone separator followed by bag filter and stack.
- 10) The treated gases shall comply with the emission standards for TOC, SO₂ and other parameters as may be prescribed by SPCBs/PCCS, then only be released in the atmosphere through dedicated stacks. The stack height shall be a minimum of 30m from ground level or as prescribed by the concerned SPCB/PCC, whichever is higher.
- 11) Treatment and disposal of wastewater: Wastewater generated from the process, excess mother liquor, floor washing, spillage, reactor washing, scrubber bleed, etc. shall be reused in the process while mixing raw materials or treated physio chemically in an ETP to comply with wastewater discharge standards and may be sent to CETP for final disposal as prescribed by SPCB/PCC. In case of zero discharge, the treated waste water from ETP may be managed as per conditions stipulated by the SPCB/ PCC.
- 12) The treated effluent shall be discharged in accordance with the conditions stipulated in the Consent to Operate issued by concerned SPCB/PCC under the Water (Prevention and Control of Pollution) Act, 1974.
- 13) The scrubbing media generated from alkali scrubber shall be reused back in process. Unit shall maintain records of scrubbing media reused.
- 14) The hazardous wastes such as floor scrapping /sweepings if any generated shall be collected and temporarily stored in non-reactive drums/ bags category wise under a dedicated hazardous waste storage area having proper caution sign and be sent to authorized common TSDF or other authorized facility within 90 days from the generation of the waste in accordance with the authorization issued by the concerned SPCB/PCC. Such storage area shall be covered with proper ventilation.
- 15) The unit shall ensure that the said utilization process and its associated activities shall be demarcated separately within premises.
- 16) The unit shall ensure that the Spent Sodium Sulphite is procured from the industries, which have valid authorization from the concerned SPCB/PCC as required under HOWM Rules, 2016.
- 17) Transportation of Spent Sodium Sulphite shall be carried out by sender (generator) or receiver (utilizer) only after obtaining authorization from the concerned SPCB under

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- Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016. Requisite manifest document shall be followed as laid down under the said Rules.
- 18) Prior to utilization of Spent Sodium Sulphite, the unit shall obtain authorization for collection, storage and utilization of Spent Sodium Sulphite from the concerned SPCB/ PCC under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.
 - 19) The unit shall maintain proper ventilation in the work zone and process areas. All personnel involved in the plant operation shall wear proper personal protective equipment (PPE) specific to the process operations involved and type of chemicals handled as per Material Safety Data Sheet (MSDS). The safety precautions of the worker shall be in accordance with the Factory Act, 1948, as amended from time to time.
 - 20) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
 - 21) In case of environmental damages arising due to improper handling of hazardous wastes including accidental spillage during generation, storage, processing, transportation and disposal, the occupier (sender or receiver, as the case may be) shall be liable to implement immediate response measures, environmental site assessment and remediation of contaminated soil / groundwater / sediment etc. as per the "Guidelines on Implementing Liabilities for Environmental Damages due to Handling & Disposal of Hazardous Wastes and Penalty" published by CPCB.
 - 22) During the process of utilization and handling of hazardous waste the unit shall comply with requirement in accordance with the Public Liability Insurance Act, 1991 as amended, wherever applicable.

109.4 Product Usage / Utilization

- 1) The end use of product "Sodium bi sulphite" derived utilizing Spent Sodium Sulphite shall be allowed for industrial use in dyes & dye intermediates, textile, and pulp & paper industries as reducing/bleaching agents and be restricted for use in food, pharma, cosmetic & fertilizer sector.
- 2) The end use of dyes dye intermediates manufactured using the above-said product (Sodium bi sulphite derived utilizing Spent Sodium Sulphite) shall not be used in any form in the food, pharma, and cosmetics sector.
- 3) The Sodium bi sulphite manufactured by utilizing Spent Sodium Sulphite shall comply with the Bureau of Indian Standards (BIS) or other respective regulatory standards, for further respective utilization.
- 4) The unit shall label its product i.e. Sodium bi sulphite prepared by utilizing Spent Sodium Sulphite as "*This Sodium bi sulphite has been prepared by Utilization of Spent Sodium Sulphite {generated during caustic scrubbing of SO₂ from Pesticide/ Dye & Dye intermediates/ Pharmaceutical sector/ Organic Chemical sector during Chlorosulphonation reactions*".



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109.5 Record>Returns Filing

- 1) The unit shall maintain a passbook issued by concern SPCB/PCC and maintain details of each procurement of Spent Sodium Sulphite as mentioned below:
 - Address of the sender
 - Date of dispatch
 - Quantity procured
 - Seal and signature of the sender
 - Date of Receipt in the premises
- 2) A log book with information on source and date of procurement of Spent Sodium Sulphite, date wise utilization of the same, hazardous waste generation and its disposal, etc. shall be maintained including analysis report of fugitive emission monitoring & effluent discharged, as applicable.
- 3) The unit shall maintain record of hazardous waste generated, utilized and disposed as per Form-3 & also file an annual return in Form-4 as per Rule 20 (1) and (2) of HOWM Rules, 2016, to concerned SPCB/PCC.
- 4) The unit shall submit quarterly and annual information on hazardous wastes consumed, its source, products generated or resources conserved (specifying the details like, type and quantity of resources conserved) to the concerned SPCB/PCC.
- 5) The unit shall use NHWTS to manage the manifest, enter daily records of quantity generated, disposed, etc.

109.6 Standards

- 1) Source emissions from the stack connected to reactors/ process unit shall comply with the following Emission standards or as prescribed by the concerned SPCB/PCC, whichever is stringent:

Particulate Matter	150 mg/Nm ³
Oxides of Sulphur (SO _x)	200 mg/Nm ³
Cl ₂	15 mg/Nm ³
HCl acid mist	35 mg/Nm ³

- 2) Work zone emission in the work zone area shall comply with the following standards:

PM ₁₀	5 mg/m ³ TWA* (PEL)
NO _x	9 mg/m ³ #
SO ₂	13 mg/m ³ TWA* (PEL)
H ₂ S	20 ppm #
Cl ₂	3 mg/m ³ #

*PEL - Permissible Exposure Limit.

*Time-weighted average (TWA)- measured over a period of 8 hours of operation of process.

- A ceiling limit is one that may not be exceeded for any period of time, and is applied to irritants and other materials that have immediate effects.



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- 3) Monitoring of the above specified parameters for Source emissions and Work zone emission shall be carried out quarterly for first year followed by at least annually in the subsequent year of utilization. The monitoring shall be carried out by ISO 17025 accredited or EPA, 1986 approved laboratories and the results shall be submitted to the concerned SPCB/PCC on a quarterly basis.
- 4) Standard for wastewater discharge: Treated effluent shall be discharged in accordance with the conditions stipulated in Consent to Operate issued by concerned SPCB/PCC under the Water (Prevention and Control of Pollution) Act, 1974. In case of (i) zero discharge as per consent or (ii) non-availability of the common Effluent Treatment Plant (CETP), the unit shall achieve zero discharge by setting up adequate captive treatment facility.

109.7 Siting of Industry

Facilities for utilization of Spent Sodium Sulphite shall be preferably located in a notified industrial area or industrial park/estate/cluster and in accordance with Consent to Establish issued by the concerned SPCB/PCC.

109.8 Size of Plant and Efficiency of Utilisation

1 MT of Spent Sodium Sulphite used as raw material yields around 1.5 MT of Sodium Bi Sulphite. Therefore, requisite facilities of adequate size of storage shed and other plant & machineries shall be installed accordingly.

109.9 Online detectors/ Alarms/ Analyzers

In case of continuous process operations, online emission Analyzers for PM, SO₂, & NO_x in the stack shall be installed and the online data be connected to the server of the concerned SPCB/ PCC.

109.10 Checklist of Minimal Requisite Facilities:

S. No	Particulars
1.	Dedicated storage area for storage of spent sodium sulphite bags or containers with proper cover, acid proof brick lining, proper slope and collection pit.
2.	Cool, dry well-ventilated covered sheds for Spent Sodium Sulphite storage tanks, product storage tanks and process activities within premises and dedicated hazardous storage area for temporary storage of hazardous waste generated during utilization process.
3.	A suitable mechanized system for handling & transfer of Spent Sodium Sulphite.
4.	Reaction vessel
5.	SO ₂ gas generator unit.
6.	Fixed pipes for transferring of sulphur dioxide gas.
7.	Fume extraction system followed by APCD with alkali scrubber connected with reaction vessel

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8.	Alkali scrubber of adequate capacity
9.	Online analyzers for PM, SO ₂ , emission monitoring in the stack, in case of continuous process operations.
10.	Settling tank
11.	Centrifuge unit
12.	Dryer unit with Hot air generator
13.	APCDs connected with dryer unit preferably the bag filters.

