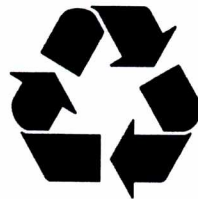


**Standard Operating Procedure and Checklist of Minimal  
Requisite Facilities for utilization of hazardous waste  
under Rule 9 of the Hazardous and Other Wastes  
(Management and Transboundary Movement) Rules, 2016**

**Utilization of Spent Phosphoric Acid generated during  
manufacturing of Quinacridone Pigment, for production of  
Dibasic Calcium Phosphate**



September, 2017

**Central Pollution Control Board**  
**(Ministry of Environment, Forest & Climate Change, Government of India)**  
**Parivesh Bhawan, East Arjun Nagar,**  
**Shahdara, Delhi – 110032**

**Procedure for grant of authorisation by SPCBs/PCCs for utilization of Hazardous Waste**

- (i) While granting authorisation for utilization of hazardous wastes, SPCBs/PCCs shall ensure the following:
- The waste (intended for utilization) belongs to similar source of generation as specified in SoPs.
  - The utilization process is similar to the process of utilization described in SoPs.
  - End-use / product produced from the waste shall be same as specified in SoPs.
  - Authorisation be granted only after verification of utilization process and minimum requisite facilities as given in SoPs.
  - Issuance of passbooks (similar to the passbooks issued for recycling of used oil, waste oil, non-ferrous scrap, etc.) for maintaining records of receipt of hazardous wastes for utilization.
- (ii) After issuance of authorization, SPCB shall verify the utilization process, checklist and SOPs on quarterly basis for initial 2 years; followed by random checks in the subsequent period for atleast once a year.
- In-case of lack of requisite infrastructures with the SPCB/PCC, they may engage 3<sup>rd</sup> party institutions or laboratories having EPA/NABL/ISO17025 accreditation/recognition for monitoring and analysis of prescribed parameters in SoPs for verification purpose.
- (iii) SPCBs shall provide half yearly updated list of units permitted under Rule 9 of Hazardous & Other Wastes (Management & Transboundary Movement) Rules, 2016 (HOWM Rules, 2016) to CPCB and also upload the same on SPCB website, periodically. Such updated list shall be sent to CPCB on a half yearly basis i.e by July and January respectively.
- (iv) Authorisation for utilisation shall not be given to the units located in the State/UT where there is no Common TSDF, unless the unit ensures authorised captive disposal of the hazardous waste (generated during utilisation) or its complete utilisation or arrangement of sharing with any other authorised disposal facility.
- (v) In case utilization proposal is not similar 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 utilization studies and developing SoPs thereof.
- (vi) The source and work zone standards suggested in the SoPs are based on the E(P)A notified and OSHA standards respectively, however, SPCB/PCC may impose more stringent standards based on the location or process specific conditions.

**39.0 Utilization of Spent Dilute Phosphoric Acid**

<b>Type of HW</b>	<b>Source of generation</b>	<b>Recovery/Product</b>
Spent Dilute Phosphoric Acid (Category No. 26.3 of schedule-I of HOWM Rules, 2016)	Generated during Cyclization process in manufacturing Quinacridone (Dye & Dye Intermediate)	Dibasic Calcium Phosphate (IP grade)

**39.1 Source of Waste**

Spent Phosphoric Acid is generated during Cyclization reaction of Di AnilinoTerephthalic Acid with Phosphoric Acid (85 %) and Phosphorus pentoxide for manufacturing Quinacridone (Violet 19 and Red 122). Due to ring closing in the cyclization reaction, water is generated and it is absorbed by conc. Phosphoric Acid. Water is added to precipitate the product (Quinacridone) and spent phosphoric acid (24 - 30 %) is generated.

Spent Phosphoric Acid is categorized as hazardous waste at S.No. 26.3 of Schedule-I of the HOWM Rules, 2016, which are required to be disposed in accordance with authorization condition, when not utilized.

**39.2 Utilisation Process**

The said hazardous waste i.e Spent Phosphoric Acid (Conc. 24 – 30 %) having pH 1-2 is neutralized with lime and water (recycled/fresh) to increase the pH to 2.8 in the reaction tank - I in the Neutralization tank. The reaction mixture is continuously agitated using agitator for about 15 – 20 minutes. The reaction mixture is passed through a nutsche filter and transferred to the intermediate storage tanks.

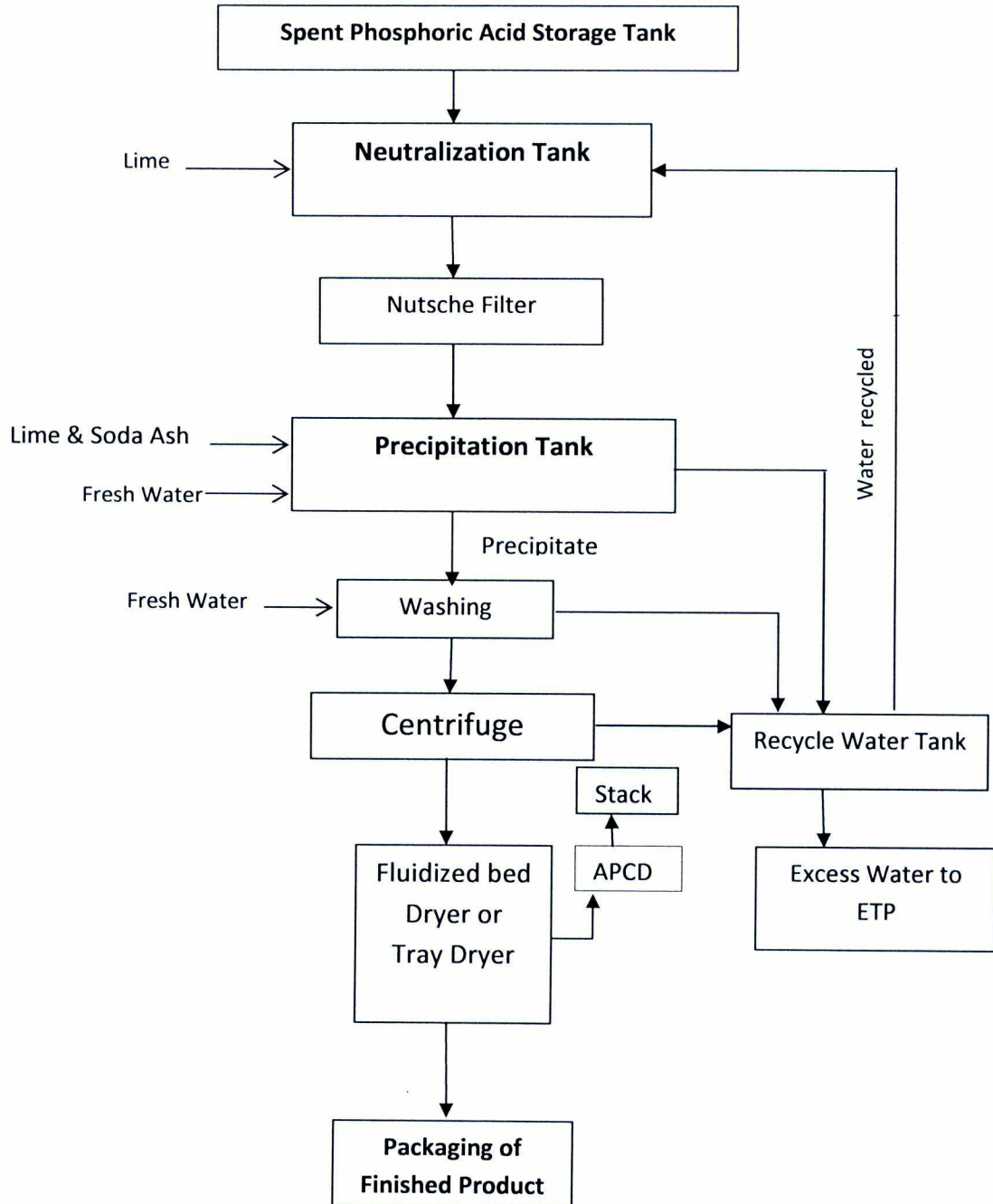
The reaction mixture is then transferred to reaction tank - II, where lime and soda ash (both in slurry form) is added to increase the pH to about 7 and agitated vigorously for one hour. The reaction mixture is allowed to settle for 20-25 minutes and the precipitate is washed with fresh water in Nutsche filter. The moisture content in the precipitate / solid mass is removed in the centrifuge, followed by drying in Fluidized Bed Dryer / Tray Dryer.

Reject liquor generated from reaction tank - II, wash water from Nutsche filter and supernatant of the centrifuge are collected in the Recycle Storage Tank. The liquor from the recycle storage tank is recycled back in the reaction tank - I. The reject water from the process is to be managed in accordance with conditions stipulated under the Consent to Operate granted by the concerned SPCB/PCC.

The Flow chart of the utilization process is provided as below;

*P.V.S*

Fig 1. Flow diagram of Utilization of Spent Phosphoric Acid for manufacturing Dibasic Calcium Phosphate



P.K.S

### 39.3 Product Usage / Utilization

The Dibasic Calcium Phosphate manufactured from the above utilization process, may be utilized as dilute/excipient for compression of tablets, substitute for lactose in tablet and capsule formulation, source of calcium and phosphorus in nutritional supplements and anti caking agent. However, the same shall meet with standards prescribed by Indian Pharmacopoeia (IP) for manufacturing of IP grade and be certified by Food and Drug Administration.

### 39.4 Standard Operating Procedure for utilization

This SoP is applicable only for utilization of Spent Phosphoric Acid (24 – 30 %) generated during manufacturing of Quinacridone pigment (Dye & Dye Intermediate Industry), as a raw material for manufacturing of IP grade Di basic Calcium Phosphate.

- (1) Spent Phosphoric Acid shall be transported in SPCB/PCC authorized acid-proof tankers mounted on vehicles fitted with requisite safeguards ensuring no spillage of the same.
- (2) There should be a designated space for unloading of Spent Phosphoric Acid into a rubber lined storage tank. The receiving storage tank shall be placed above the ground and contained with low raise parapet/bund wall & acid proof floor with slope to collect spillages, if any, into collection pit.
- (3) The unit shall install storage tank under cool, dry well-ventilated covered storage shed(s) with in premises, as authorized by the concerned State Pollution Control Board/Pollution Control committee under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016 so as to eliminate rain water intrusion.
- (4) There shall be no manual handling of the hazardous waste (Spent Phosphoric Acid). Acid Proof pump shall be used for transfer of Spent Sulphuric Acid through pipelines to the reaction vessels.
- (5) Such storage sheds for chemicals (like lime, soda ash) shall have impervious lined floor, adequate slope and seepage collection pit. The loading/unloading space for chemicals shall also be under the covered shed.
- (6) The entire process area shall have leak-proof and acid proof tiles with adequate slope to collect spillages, if any, into a collection pit. The spillages from collection pit shall be transferred to ETP or reaction tanks, as the cases may be, through chemical process pump.
- (7) The unit shall provide separate storage tanks for storage of chemicals and the storage tanks should be at designated place with proper cover and with acid brick lining floors.

- (8) Spent Phosphoric Acid shall be mixed with lime and water in closed vessel reactors (neutralization reactor) having mechanized stirring system with reaction time of 15-20 minutes. The mixer shall be kept under covered shed with adequate safety gadgets provided to workers, as well as ensuring proper ventilation in the process area.
- (9) There shall be a closed lime slurry preparation system with mechanical mixing facility so as to avoid fugitive dust emission.  
The lime slurry shall be transferred to Neutralization & Precipitation tank mechanically using piping arrangement.
- (10) In precipitation tank, the reaction mass from neutralization tank be transferred mechanically using acid proof pumps. The reaction mass be precipitated using fresh water, lime and soda ash. The precipitation tank shall have mechanized stirring system for mixing (about one hour) under covered shed with adequate safety gadgets provided to workers, as well as ensuring proper ventilation in the process area. After mixing, the precipitated mass shall be allowed to settle for about 15-20 minutes.
- (11) Both the tanks (i.e. precipitation tank and neutralization tank) shall be made up of acid proof material like HDPE.
- (12) The precipitate (i.e. Dibasic Calcium Phosphate) from the precipitation tank shall be washed using fresh water in filter press like arrangement or other suitable arrangement.
- (13) The fluid bed dryer/tray dryer shall be operated using natural gas permitted by the concerned SPCB/PCC. The dryer shall be attached with Air Pollution Control Devices (APCD) like Bag house filter to meet with the prescribed standards.
- (14) The product i.e. Dibasic Calcium Phosphate shall meet with standards prescribed by Indian Pharmacopoeia (IP) for manufacturing of IP grade and be certified by Food and Drug Administration.  
The product shall also be labeled as “This product is manufactured using spent phosphoric Acid generated from manufacturing of Quinacridone (Dye & Dye Intermediates)”.
- (15) 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) such as chemical goggles, full-face shield, or a full-face respirator, impervious gloves of chemically resistant material (rubber or neoprene), body suits, aprons, and/or coveralls of chemical resistant material and impervious boots of chemically resistant material. The safety precautions of the worker shall be in accordance with the Factory Act, 1948, as amended from time to time.

- (16) Treatment and disposal of wastewater: Process waste water generated during utilization process (such as excess recycled waste water or from precipitation/centrifuging, product washing, etc.) shall be treated in a suitable Effluent Treatment Plant (ETP) so as to meet standards/conditions as specified by concerned SPCB/PCC.
- (17) It shall be ensured that Spent Phosphoric Acid is procured from the industries that have valid authorization for the same from the concerned SPCB/PCC as required under Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.
- (18) The hazardous waste generated (ETP sludge, Nutsche filter residue, wash residue product spillages, etc.) shall be collected and temporarily stored in non reactive drums / bags under a dedicated hazardous waste storage area and be sent to authorized common TSDF or other authorized facility within 90 days from generation of the waste in accordance with the authorization issued by the concerned SPCB/PCC. Such storage area shall be covered with proper ventilation.
- (19) Transportation of Spent Phosphoric Acid and residues generated during utilization shall be carried out by the sender or receiver (utilizer/TSDF operator) as per the authorization issued by concerned SPCB/PCC under the Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016, with requisite safeguards ensuring no pilferage of the wastes.
- (20) Prior to utilization of spent Phosphoric acid, the unit shall obtain authorization for generation, storage and utilization of Spent phosphoric acid from the concerned State Pollution Control Board under the Hazardous and Other wastes (Management & Transboundary Movement) Rules, 2016.
- (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 unit 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) The unit shall provide suitable fire safety arrangements and flame proof electrical fittings.
- (23) The hazardous wastes (i.e ETP sludge, Nutsche filter residue, wash residue product spillages, etc.) generated during the said utilization process shall be disposed in captive or common hazardous waste disposal facility as authorized by concerned SPCB/PCC in accordance with the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016. In case, standard operating procedures / guidelines have been developed by CPCB for

utilization/recycling of the said hazardous waste, the same may be utilized/recycled at authorized facility in accordance with the said rules.

- (24) During the process of utilization and handling of hazardous waste, the unit shall comply with the requirements in accordance with the Public Liability Insurance Act, 1991 as amended, wherever applicable.

### 39.5 Record/Return Filing

- (1) The unit shall maintain a passbook issued by concerned SPCB wherein the following details of each procurement of Spent Phosphoric Acid shall be entered:
- 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 the said hazardous waste, quantity, date wise utilization of the same, quantity of dibasic calcium phosphate manufactured, hazardous waste generation and its disposal etc. shall be maintained including analysis report of emission monitoring & effluent discharged, as applicable.
- (3) The unit shall maintain record of hazardous waste utilized, hazardous waste generated and disposed as per Form 3 & shall file annual returns in Form 4 as per Rule 20(1) and (2) of the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016, to concerned SPCB.
- (4) The unit 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.

### 39.6 Standards

- (i) Source Emissions from the stack connected to Fluid bed dryer / Tray dryer shall comply with the following standards or as prescribed by the concerned SPCB/PCC, whichever is stringent:

PM	: 50 mg/Nm <sup>3</sup>
TOC	: 20 mg / Nm <sup>3</sup>

Note: Other parameters as prescribed by SPCB/PCC, if any, shall be complied.

- (ii) Fugitive emissions in the work zone shall comply with the following standards:

PM <sub>10</sub>	– 5 mg/m <sup>3</sup> TWA* (PEL)
Phosphoric Acid	– 1 mg/m <sup>3</sup> TWA* (PEL)

\*PEL – Permissible Exposure Limit

- (iii) Monitoring of the above specified source emission parameter shall be carried out quarterly. The monitoring shall be carried out by NABL accredited or ISO17025 /EPA approved laboratories and the results shall be submitted to the concerned SPCB/PCC on a quarterly basis.



- (iv) Standards for wastewater discharge: The treated waste water shall be discharged in accordance with the conditions stipulated in the Consent to Operate issued by respective SPCB/PCC under the Water (Prevention and Control of Pollution) Act, 1974. In case of zero discharge or no discharge condition stipulated in the said Consent or non-availability of the Common Effluent Treatment (CETP), zero discharge shall be met.

**39.7 Siting of Industry**

Facilities for utilization of Spent Phosphoric Acid from the generated during manufacturing of Quinacridone pigment (Dye & Dye Intermediate Industry) shall be located in a notified industrial area or industrial park/estate/cluster and cited in accordance with Consent to Establish issued by the concerned SPCB/PCC.

**39.8 Size of Plant & Efficiency of utilisation**

100 Kg of Spent Phosphoric Acid yields about 38-39 Kg of Dibasic Calcium Phosphate. Hence, requisite facilities of adequate size shall be installed accordingly as mentioned under para 39.10 below.

**39.9 On-line detectors / Alarms / Analysers**

In case of continuous process operations, online analysers shall be installed for acid mist in the stack emission connected to dryer. The on-line data be connected to the concerned SPCB/PCC server.

**39.10 Checklist of Minimal Requisite Facilities:**

S.No	Requisite Facilities
1.	Storage tank(s) of adequate capacity to store Spent Phosphoric Acid within the premises. Such storage tank(s) shall be made up of acid proof material and be placed above the ground and contained with low raise parapet/bund wall & acid proof with slope to collect spillages, if any, into collection pit.
2.	Cool, dry, well-ventilated covered storage shed(s) for the aforesaid Spent Phosphoric Acid storage tanks.
3.	Chemicals shall be stored in non-reactive drums/containers in cool, dry, well ventilated and covered storage shed so as to eliminate water intrusion. The storage shed shall have impervious lined floor and have adequate slope with seepage collection pit.
4.	The process area shall have proper ventilation (preferably with ventilation ducts above the process units).
5.	Dedicated covered hazardous waste storage area to store hazardous

**Standard Operating Procedure and Checklist of Minimal Requisite Facilities for Utilization of Spent Phosphoric Acid generated during manufacturing of Quinacridone Pigment, for production of Dibasic Calcium Phosphate**

	generated during utilization process.
6.	Neutralization Tank and Precipitation Tank of adequate size made up of acid proof material like HDPE
7.	Intermediate Storage tanks of adequate size made up of acid proof material like HDPE
8.	Nutsche filters
9.	Filter press like arrangement or other suitable arrangement for washing of precipitate
10.	Centrifuge
11.	Fluid bed Dryer / tray dryer (operated using fuel such as natural gas as permitted by the concerned SPCB/PCC)
12.	Recycling Water Tank
13.	Bag filter house or other suitable APCD attached to Fluid bed Dryer / tray dryer followed by stack of minimum height of 6 m above the roof top or as prescribed by the concerned SPCB/PCC, whichever is higher
14.	Stacks to have sampling port, platform, access to the platform etc. as per the Guidelines on Methodologies for Source Emission Monitoring published by CPCB under Laboratory Analysis Techniques LATS/20/2013-14.
15.	Effluent treatment plant or other waste water management system so as to meet discharge standards/conditions prescribed by the concerned SPCB/PCC

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