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CALS-technology for Production of Dibasic Lead Phosphite in Phosphoric Sludge Utilization

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Phosphoric sludge is the most harmful and dangerous of waste of phosphorus-containing substances, and its aggregated volumes, by rough estimates, total millions of tons. Therefore utilization of the that waste is now an acute problem and will bring rather notable contribution not only to national economies, but will also considerably improve ecological conditions (Bessarabov et al., 2010a).
Development of industrial productions for processing of phosphoric sludge was carried out within the most modern and prospective system of computer support - CALS-technologies (Continuous Acquisition and Life Cycle Support). The task of the CALS is transformation of product life cycle to highly automated process by re-structuring of business processes included into it (Saaksvuori, Immonen, 2010).
In development of advanced chemical productions it is shown that CALS-technologies and the main CALS-standard, ISO 10303 STEP, offer of a solution of a problem of electronic representation of the design information by means of use of the standardized integrated description of a product. The designer's electronic description according to standard ISO 10303 STEP contains structure of categories, documents, statuses, groups of products with their versions, properties, classifications, etc (Molina et al., 1999).
Marketing researches of the phosphoric industry waste utilization (Bessarabov et al., 2010b), system researches of innovative resources of leading enterprises making and utilizing phosphorus-containing production wastes (Bessarabov et al., 2010c) were carried out within the grant of European Community ECOPHOS № INCO-CT-2005-013359, and also the flexible two-product scheme of phosphoric sludge utilization with obtaining of sodium phosphite and hypophosphite (Bessarabov et al., 2009, Klemeš et al., 2006) was developed.
In the given work carried out under the contract of Ministry of Education and Science of Russia no. 11.519.11.5005, we considered the complex of three individual productions flowsheets of phosphoric sludge utilization, including sodium phosphite and hypophosphite, and also phosphoric sludge processing through sodium phosphite to dibasic lead phosphite.

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1. Development of the flexible three-product scheme for utilization of phosphoric sludge for the obtaining of dibasic lead phosphite

Dibasic lead phosphite ($2PbO \cdot PbHPO_3 \cdot 0,5H_2O$) is used for the stabilization of polyvinyl chloride. The share of the lead salts in the total production of stabilizers is 75 %. In recent years, the most perspective stabilizers are tribasic lead sulphate and dibasic lead phosphite.

The composition and structure of dibasic lead phosphite is suitable for stabilizing chlorinated polymers such as polyvinyl chloride, as it also imparts resistance to heat and light to the plastic (Daniels et al., 2005). A high percentage of lead in a basic salt ensures a sufficiently high stability which is superior to other stabilizers to this indicator. It is used in products, which should be resistant to atmospheric influences. Also, dibasic lead phosphite is used in rigid and plasticized cable compositions based on polyvinyl chloride. Dibasic lead phosphite is superior to other known lead salts on the photoresist effect, and has antioxidant properties. It is used in small quantities and at relatively low temperatures. (< 200°C). Dibasic lead phosphite is often used in mixtures with tribasic lead sulphate to improve the color of products and to stabilize it (Sims and Sharpley, 2005).

The advantage of dibasic lead phosphite is its low cost, but its significant disadvantage is high toxicity, so there is a tendency to avoid the use of powdered forms. This is achieved by pelleting, treatment of surface by oils, fatty acids or their salts, dispersion in plasticizers, creation of the liquid stabilizers.

In the production of dibasic lead phosphite sodium phosphite, obtained in a flexible two-product production (Bessarabov et al., 2009b), is used as a raw material. Therefore, we developed a flexible three-product scheme for processing phosphoric sludge (Figure 1). This scheme allows to combine three productions, namely, sodium phosphite and hypophosphite, and dibasic lead phosphite.

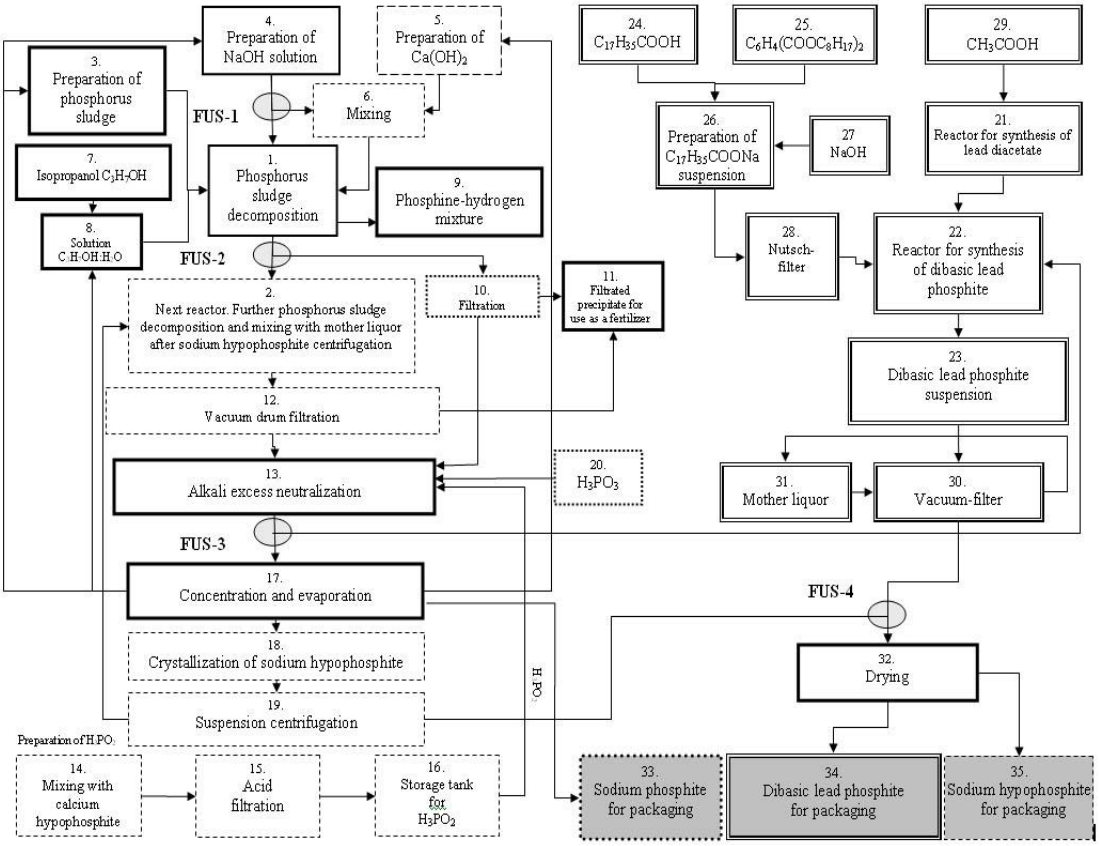

Figure 1. The flexible technology for production of sodium phosphite, sodium hypophosphite and dibasic lead phosphite

To combine these individual productions the principles of the flexibility theory were used. Flexible three-product production corresponds to two features of the theory of flexible chemical engineering systems, i.e. has the technological and chemical similarity. If we consider the technological similarities, at the design stage specific blocks for the flexible two-product production were allocated (flexible units of switching: FUS-1 and FUS-2) as well as new FUS-3 and FUS-4 that allow the production of required products with minimal control actions.

At the unit FUS-1 one can switch streams either directing NaOH (predetermined concentration) from step (4) directly into the reactor (1) during the production of sodium phosphite, or to step (6) to be mixed with $Ca(OH)_2$ in the production of NaH_2PO_2. After the reactor (1) in the FUS-2 unit, there is either switching to the stage (10) for filtering the resulting reaction mixture in the case of Na_2HPO_3, or switching to step (2), where further decomposition of phosphorus sludge and mixing the mother liquor begins during the obtaining of NaH_2PO_2.

At the FUS-3 unit one can switch streams either directing the solution of Na_2HPO_3 (13) after the step of neutralizing alkali excess in the stage (22) in the synthesis reactor in the production of dibasic lead phosphite, or in the stage (17) for concentration and evaporation in the production of Na_2HPO_3. For FUS-4 unit, there is a switch to the drying step (32) or after step (19), centrifuging the suspension NaH_2PO_2, to the stage (30) (drum vacuum filter) in the production of dibasic lead phosphite.

Units of flexibility allow to switch the process stream (based on the order or demand for the final product) for the production of Na_2HPO_3 or NaH_2PO_2. There is also the possibility of reducing of production time by one-time obtaining of Na_2HPO_3 and NaH_2PO_2. This technology provides the ability to reduce the size of the room in which the production is situated, because many technological units (production of Na_2HPO_3 and NaH_2PO_2) are combined.

For the three-product flexible production in the preparatory stage, phosphorus sludge is pulverized in crushers to a particle size optimal for interaction with NaOH, and then a solution is prepared. We divided the production process in 18 following steps :

1. Preparation of calcium hydroxide solution. In the tank (5) parallel to the crushing of the phosphoric sludge a process of preparing $Ca(OH)_2$ by dissolving CaO in water to a concentration of 65% is carried out.
2. Preparation of NaOH solution. This step (4) as analogous to the preparation stage of NaOH in the production of sodium phosphite (Strugatskaya et al., 1994). The alkali is diluted to a concentration of 45%, using water as a solvent. Then the obtained solutions of NaOH and $Ca(OH)_2$ are to be mixed at the tank (6).
3. The decomposition of phosphorus sludge in the reactor (1). Sludge from (3) is loaded into the reactor, together with the solution from the tank (6). After some time the $CH_3CH(OH)CH_3$ solution (7), required for a more complete extraction of phosphorus from the sludge, is put to the reactor. At the same time phosphine-hydrogen mixture is removed from the reactor. The stage of sludge decomposition is typical both for the production of Na_2HPO_3 and NaH_2PO_2.
4. After passing step (1) (decomposition of sludge) FUS-1 switches the solution feed either on the stage (10) (filtering, in the production of Na2HPO3), or on stage (2) in the production of NaH_2PO_2.
5. Further decomposition of the sludge in additional reactor (2). From the reactor (1) the mixture is directed into the reactor (2) while mixing with the mother liquor after centrifuging of NaH_2PO_2. After completion of the reaction, the solution of an additional reactor (2) enters the drum vacuum filters (12). The stage is typical only for the production of NaH_2PO_2.
6. Filtering in drum vacuum filters for the preparation of NaH_2PO_2. The resulting solution from the reactor (2) is filtered in a drum vacuum filter (12). The precipitate formed during filtration, removed and used as fertilizer in the agricultural industry (Klemeš, 2010). The solution passed through a vacuum filter (12) goes to the neutralizer (13).
7. Neutralization of NaOH excess. After passing through the drum vacuum filter, the solution consisting of NaH_2PO_2 (8 %), Na_2HPO_3 (9 %) and $CaHPO_3$ (25 %) goes to the neutralizer (13). Neutralization of NaOH excess is carried out by the diluted H_3PO_2, located in the tank (16). The stage of neutralization is typical both for the production of Na_2HPO_3, and NaH_2PO_2.
8. Preparation of H_3PO_2. The finished product ($Ca(H_2PO_2)_2$) with a concentration of 12 % is mixed with the oxalic acid. The resulting solution is filtered (15) and the resulting hypophosphorous acid is stored in the tank (16). As necessary, using at the neutralization step (13).

9. The concentration of NaH_2PO_2 and sodium phosphite. In step (17) NaH_2PO_2 is concentrated (by evaporation) for the further fine filtration, which is carried out in step (18). In this case the resulting sodium alkali and NaH_2PO_2 are sent to recycling. Sodium phosphite after passing the stage (17) through the FUS-3, goes to the packaging (33).
10. Crystallization of NaH_2PO_2 (18) and centrifugation of the suspension (19). After passing through the stage of crystallization (18), the suspension goes to the centrifuge. The resulting mother liquor is recycled via the optional reactor (2). After centrifugation step (19) NaH_2PO_2 is dried (32) to remove excess moisture from the product. This stage is controlled by the FUS-4, which performs switching the feed of raw materials from step of centrifugation (19), or from step of the vacuum filtering (30).
11. After implementation of the main production cycle after the step of drying (32), NaH_2PO_2 goes to packaging (20).
12. Preparation of Na_2HPO_3 solution. A solution of Na_2HPO_3 comes from the stage (13) by the pipeline and sends to the dibasic lead phosphite synthesis reactor (22). If necessary, pH is adjusted with acetic acid.
13. Preparation of sodium stearate solution (soap). Solution of $C_{17}H_{35}COONa$ is prepared in device (26). The device is filled by the freshly prepared solution of NaOH (27) with a concentration of 1.4 g/l. NaOH solution is heated to 90-95°C and under energetic hand stirring load the stearin (24) through the hatch. Saponification reaction passes in 20-30 minutes. Finished soap solution should contain a slight excess of NaOH. In order to eliminate the dusting of the product, dioctyl phthalate is added to the final solution of soap (25), and the solution is stirred for another 10 min, maintaining the temperature at 85-90°C.
14. Synthesis of $PbO{\cdot}Pb(CH_3COO)_2$ is carried out in the unit 21. Turn the mixer, heat to 60 °C, then the acetic acid is loaded through the loading hatch (29). The solution is stirred for 1.5-2 h with maintaining the temperature of 60 °C in the device. In the reactor, the reaction occurs:
$3PbO + CH_3COOH \rightarrow 2PbO{\cdot}Pb(CH_3COO)_2{\cdot}0.5H_2O + 0.5\ H_2O$
with the formation of dibasic lead diacetate. The solution is cooled to 20 °C and sucked down in the device (22).
15. Obtaining of hydrophobized dibasic lead phosphite. Solution of Na_2HPO_3 is added to the stirred dibasic lead diacetate solution in the device at 20°C (21). At the same time hot solution of sodium stearate is filled through the hatch (26). Dibasic lead phosphite suspension is poured to device (23).
16. Filtration of the suspension. Filtration of the suspension is carried out in the vacuum drum filter with the filter surface area of 1 m^2 (30). Calico and perchlorovinyl cloth (below – two layers of calico, above – a layer of perchlorovinyl cloth) are used as the filter cloth, as well as filtermitcal or belting can be used as the filter material. From the device (23) suspension under continuous stirring self-flows to the trough of the drum vacuum filter (30). The excess of suspension from the trough returns back to the device (23) by the pump through the overflow connecting pipe. Filtration of the suspension and the stripping of sediment are produced continuously. The pressed product is cut with a drum vacuum filter knife and poured by the closed tray to the reception container (plastic bag). The mother liquor is sucked down alternately to the storage tanks (31).
17. The drying of the product – paste of dibasic lead phosphite is conducted by the hot air in the two devices (32) of the "fluidized bed" type and bicylindroconical form. Paste of the product with a moisture content of 35-40 % is loaded into a hopper where it is fed through the grid (square = 0.05 m^2) by the means of the auger. The final product is put into a hopper, from which every 30-40 min unloading and packing are done (34).
18. After the implementation of the main production cycle after the drying step (32), dibasic lead phosphite is sent to packaging (20).
The technology developed allows to obtain three final products at once from the phosphoric sludge: sodium hypophosphite and phosphite, as well as dibasic lead phosphite. And application of principles of flexible production can increase the effectiveness of this technology.

2. CALS-project of the flexible three-product technology for the obtaining of dibasic lead phosphite

The main attention when considering the product life cycle stages in the CALS (marketing, design, production, sale and use) was paid to the design. For the most important design phase "Initial data for design" (IDD) final database chart have been developed, called in the CALS standard (ISO 10303) as "application protocols (rules)" These protocols are standard solutions in the created CALS-project.

The structure of the IDD for the CALS-project consists of 17 core units: the general data on technology (01); characteristics of the carried out research and experimental work (02); feasibility study of a recommended production method (03); a patent card (04); characteristics of feedstock, auxiliary materials (05); physical and chemical constants and properties of initial, intermediate and final products (06); chemical, physicochemical bases and basic production flow sheet (07); operating technological parameters of production process (08); the mass balance of production process (09); characteristics of by-products and solid waste (10); the mathematical description of technological processes and devices (11); data for calculation, design, the choice of the basic production equipment (12); recommendations for process automation (13); the analytical control of production process (14); methods and technological parameters of purification from chemical and industrial pollutants (15); safety data sheet including fire and explosion hazard data, fire fighting procedures, health hazard data, regulatory information (16); the list of reports and recommended literature on considered technology (17).

The flexible chart developed (Figure 1) is input in the information CALS-project (Figure 2) with all technical characteristics, drawings of the used equipment, etc. The chart includes 35 chemical and technological blocks, including: 10 combined blocks used in production of dibasic lead phosphite, sodium phosphite and hypophosphite (full line); 3 blocks concerning sodium phosphite production (dotted line); 10 blocks used in sodium hypophosphite production (dashed line) and 12 blocks concerning only to production of dibasic lead phosphite (double line). FUS-1-4 allow switching from one product to another one.

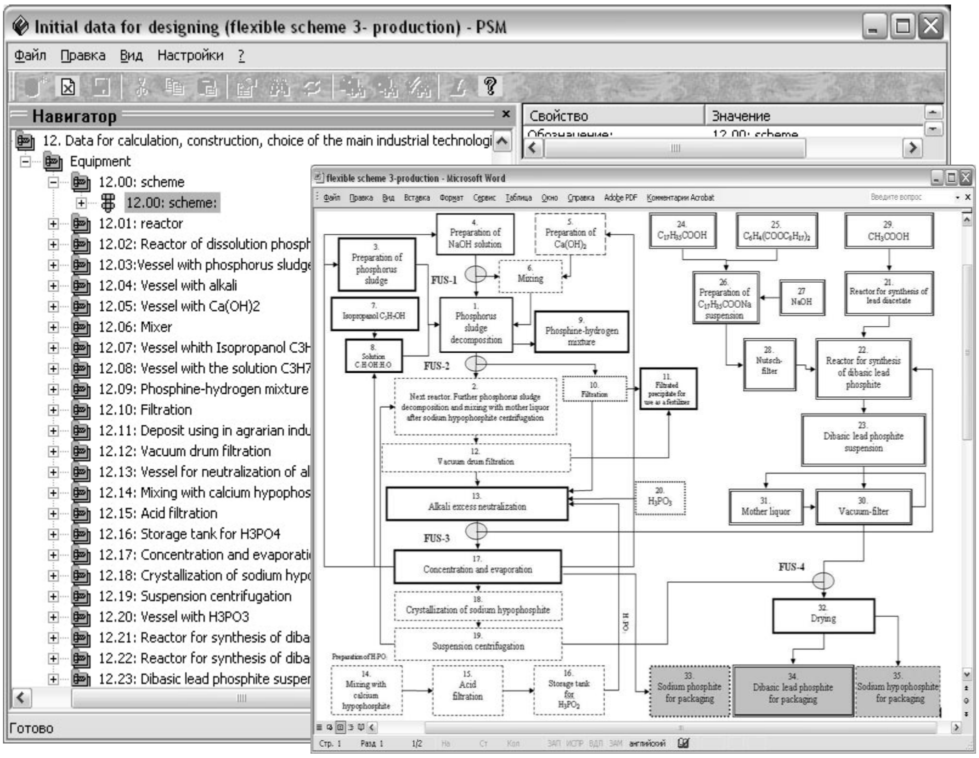

Figure 2. Element of the CALS-project "Initial data for design": the flexible three-product scheme for the phosphoric sludge processing

The present level of development of innovative products is closely related to CALS-technologies, i.e. using a common information space in all phases of product life cycle – from design and operation to utilization. The introduction of information CALS-technologies for the design of flexible of dibasic lead phosphite, sodium phosphite and hypophosphite yields not only products with high performance but also provides full after-sales support, including documentation in electronic form.
Development of design documentation was carried out using "AutoCAD". For easy storage and search time reduction, some large drawings and flowcharts were transferred to PDF-files. The same technique was used to store large text documents prepared in MS Word.

3. Conclusions

Application of CALS-technologies in the developed flexible three-product technology for processing phosphate sludge to produce the dibasic lead phosphite allows to ensure the planned product quality in an integrated system of computer support through electronic documentation of all processes of design and production technologies. The effectiveness of the technology is enhanced by the integration of information and reducing paperwork costs, re-entry and processing of information, and provides continuity of the results in complex projects.

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