

LIQUID-LIQUID TECHNIQUES IN PHOSPHORUS CHEMISTRY

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Abstract - With the aid of a number of examples ranging from phosphorus production, reactions of elemental phosphorus with caustic soda, the synthesis of organo-phosphorus halides and phosphorus sulfur compounds to the purification of wet process phosphoric acid by means of various organic solvents, it is shown how to use the existing techniques of liquid-liquid interaction in phosphorus chemistry and how to adapt them to the demands of special systems.

1. Introduction

Several processes of industrial phosphorus chemistry necessarily or advantageously use reaction media consisting of completely or partially immiscible liquid phases. In such processes simple physical operations such as cooling or separating of phases are often accompanied by chemical reactions, e.g. the formation of intermediates or final products or the extraction of impurities or valuable minor constituents from the main products. Depending on the properties of the compounds or mixtures constituting the technical systems and/or participating in processes, it is therefore necessary to vary process conditions in a wide range. Furthermore, the basic systems often have to be modified by suitable additives or other means.

2. Processes with elemental phosphorus

Liquid-liquid techniques are often indispensable in reactions with elemental phosphorus. The reason is the low solubility of liquid phosphorus in water and many other liquid phases. Carbon disulfide and aromatic compounds are the main exceptions.

2.1 Purification processes

2.1.1 Separation of undissolved impurities

Immiscible liquid phases are difficult to handle under technical conditions because they normally do not constitute pure substance systems in this case. One characteristic effect of this is the formation of multi-phase intermediate layers at the liquid-liquid interface, which is triggered by impurities. The so-called phosphorus sludge is a classic example; it forms at the phosphorus-water interface (fig. 1) during condensation of the phosphorus vapour with water when it is discharged from a phosphorus furnace, constituting a complicated physical system which consists of much phosphorus, much water, suboxides of phosphorus, silicic acid and a few other impurities. This sludge forms in large quantities in unfavourable operating conditions of the furnaces, and until recently has in many cases raised considerable problems (Ref. 1). Special automated filtration processes adapted to this difficult system of substances, and recycling of the filtration residues to suitable points of the production process have led to satisfactory solutions in the meantime.

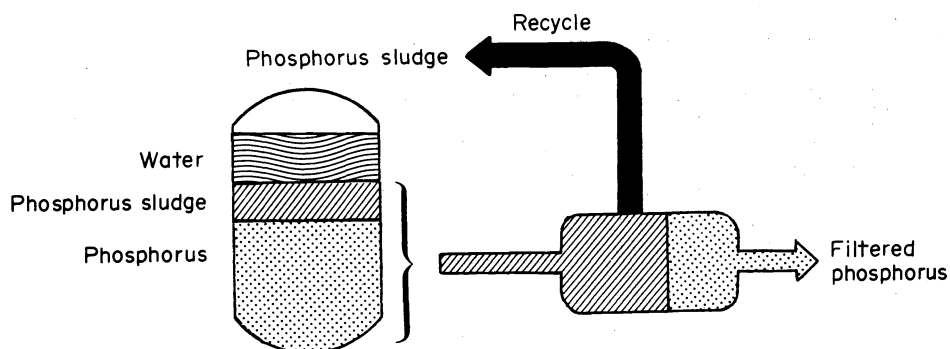


Figure 1. Purification of elemental Phosphorus by filtration

2.1.2 Separation of dissolved impurities

Despite their low solubility in elemental phosphorus considerable problems may be caused by impurities in the phosphorus during the production of derivatives. This applies, among other things, to organic impurities with preponderantly aromatic structures which, in the form of cracked products, for example, from the tar of the Söderberg electrode mass, get into the phosphorus in the dissolved state.

Purely physical removal by liquid-liquid extraction has not been industrially feasible so far, because substances which extract the organic impurities from the phosphorus themselves dissolve phosphorus in notable amounts or are themselves markedly soluble in phosphorus. For this reason, for example, the use of *o*-dichlorobenzene failed, although, as can be seen from table 1, the initial content of organic substances in the phosphorus could still be reduced by more than 75 %, even at a very small phase ratio of *o*-dichlorobenzene to phosphorus of 1:50.

The problem can be resolved if application of the liquid-liquid technique is coupled with chemical reactions. Thus these impurities can be displaced at a rate of over 90 % from the phosphorus phase into the acid phase with the aid of concentrated sulfuric acid by a series of dehydration, oxidation and sulfonation reactions (Ref. 2). At the same time there is a desirable, substantial reduction of inorganic impurities.

When employing this process on a large industrial scale it should be noted that elemental phosphorus itself can be oxidized by concentrated sulfuric acid, considerable amounts of heat being liberated; this can be seen from the ΔH -values of the reactions shown in fig. 2. From the heat of reaction aspect, particularly the reaction up to H_2S is favoured. Special precautionary and safety measures consequently have to be taken, as these reactions can build up by way of an autocatalytic effect.

Due to the small differences in density between phosphorus and sulfuric acid the subsequent phase separation is difficult (table 2). However, the density of the H_2SO_4 phase can be reduced by adding H_2O , so that residual amounts of H_2SO_4 can easily be separated as the upper phase from the phosphorus.

| | BEFORE | AFTER |
|--|--------------------------------------|--------|
| | TREATMENT (MG/100 G P ₄) | |
| <u>WITH O-DICHLORBENZENE</u> +) | | |
| ORGANIC IMPURITIES | 0,2 | 0,05 |
| <u>WITH CONCENTRATED SULPHURIC ACID</u> +) | | |
| ORGANIC IMPURITIES | 0,2 | <0,01 |
| TOTAL INORGANIC IMPURITIES | 0,15 | <0,005 |

+) RATIO PHOSPHORUS/O-DICHLORBENZENE AND PHOSPHORUS/SULPHURIC ACID APPROXIMATELY 20
t = 70°C

Table 1. Purification of elemental phosphorus

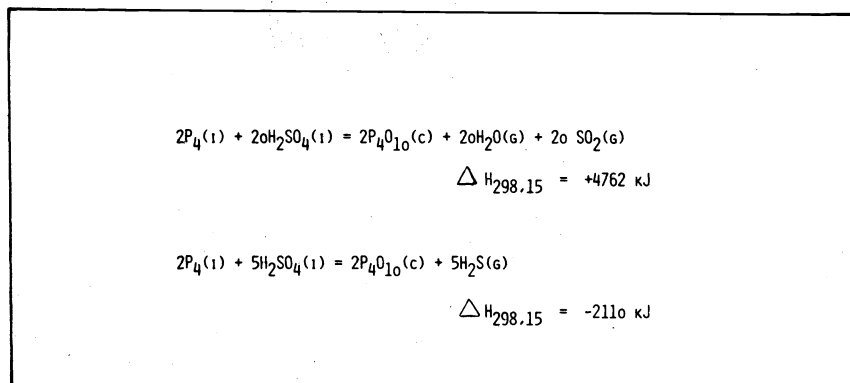


Figure 2. Oxidation of elemental phosphorus with concentrated sulfuric acid

| | | |
|---|--------|-----------------------|
| ρ H ₂ SO ₄ 96% | = 1,84 | } $\Delta\rho = 0,11$ |
| ρ P ₄ | = 1,73 | |
| ρ H ₂ SO ₄ 20% | = 1,15 | } $\Delta\rho = 0,58$ |

Table 2. Purification of elemental phosphorus with concentrated sulfuric acid (densities of the liquid phases at 60° C)

2.2 Reactions with elemental phosphorus

2.2.1 Disproportioning in alkaline medium

It is attractive for the chemist to influence the course of the reaction in the desired way and in the desired direction by means of selective variation of the composition and properties of one or both liquid phases. Disproportioning of elemental phosphorus with sodium hydroxide solution should be mentioned as an example. On the basis of the stoichiometries of the molecular reaction equations shown in figure 3, the hydrogen-producing reactions might preferably take place in the presence of excess NaOH and H₂O, calculated on the phosphorus quantity used, and the PH₃-producing reactions might preferably take place in the presence of a deficit of NaOH and H₂O. In addition it can be seen that with higher NaOH concentrations (NaOH/H₂O ratios) phosphite might preferably form and with lower NaOH concentrations preferably hypophosphite. A combination of both methods, i.e. on the one hand working with a below-stoichiometric (NaOH + H₂O)/P₄ ratio and on the other the use of as highly concentrated NaOH as possible could lead to a low hydrogen content, that is to say high-percentage PH₃, and by increased guidance in the direction of phosphite formation, to a greater PH₃ yield calculated on the phosphorus used. Optimization of the conditions showed that in fact in this way not only is a PH₃ concentration of up to 95 % attainable, i.e. with a content of only 5 % H₂, but at the same time also a PH₃ yield of up to 33 % calculated on the phosphorus used. This yield is considerably above the theoretical value of 25 % for reactions up to the hypophosphite stage (Ref. 3, 4).

The general experience was confirmed by this example, too, namely that the course of reactions in liquid-liquid phase systems can frequently be accelerated and controlled by increasing the solubility of at least one of the starting materials in the phase in which the second reactant is located. In this case long-chain higher alcohols have proved suitable, which increase the solubility of the phosphorus in the NaOH phase in which the reaction is evidently taking place.

| REACTIONS RESULTING IN PH ₃ -FORMATION | THEORETICAL PH ₃ -YIELD | COMPOSITION OF THE GASPHASE | |
|--|---------------------------------------|--------------------------------|------------------|
| | | PH ₃ % | H ₂ % |
| $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ | 25 | 100 | 0 |
| $P_4 + 4NaOH + 2H_2O \rightarrow 2PH_3 + 2Na_2HPO_3$ | 50 | 100 | 0 |
| REACTIONS RESULTING IN H ₂ -FORMATION | | | |
| $P_4 + 4NaOH + 4H_2O \rightarrow 2H_2 + 4NaH_2PO_2$ | 0 | 0 | 100 |
| $P_4 + 8NaOH + 4H_2O \rightarrow 6H_2 + 4Na_2HPO_3$ | 0 | 0 | 100 |
| EXPERIMENTAL VALUES UNDER OPTIMAL CONDITIONS | | 33 | 5 |

Figure 3. Disproportionation of elemental phosphorus with caustic soda

2.2.2 Disproportioning in acid medium

Carrying out a reaction in a liquid-liquid phase system has the disadvantage - for example, compared to the reaction of a finely dispersed solid with a liquid phase - that even with very intensive mixing the phase interface and thus also the rate of reaction is often too small for an industrial scale process. This applies, for example, to the disproportioning of phosphorus by reaction with water to phosphine and phosphoric acid. Albright & Wilson and Hooker Chemicals (Ref. 5) have developed a special liquid-liquid-solid technique for this purpose (fig. 4). Liquid white phosphorus is emulsified in phosphoric acid and first converted into very fineparticle solid red phosphorus, optimum conditions being maintained; this in turn is converted into PH₃ and H₃PO₄ in the subsequent solid-liquid reaction.

2.2.3 Further reactions with elemental phosphorus

Further examples of reacting elemental phosphorus in liquid-liquid phase systems are, among others, symproportioning of triphenyldichlorophosphorane with white phosphorus to obtain triphenylphosphine and PCl₃, a reaction which BASF (Ref. 6) employed for recycling triphenylphosphine oxide during vitamin A synthesis (fig. 5) and the production of alkali phosphides by reacting liquid sodium or sodiumpotassium alloys with liquid white phosphorus in an inert mixture of aromatics (Ref. 7) (fig. 6); this process is of interest from the technological aspect. Because of its notable dissolving power for elemental phosphorus this third liquid phase used as a continuum enables the reaction to take place via the liquid phase. On the other hand, however, it makes it possible to attain an appropriate dilution of the reaction medium and absorption and dissipation of the large amounts of heat that are liberated. But it has not yet been used on an industrial scale.

3. Liquid-liquid techniques with wet-process phosphoric acid

During recent years the most important impulses were imparted to liquid-liquid phase techniques in phosphorus chemistry by the development of separating processes in the area of wet-process phosphoric acid technology right up to the industrial production stage. On the one hand, purification of wet-process phosphoric acid to nearly the quality standard of thermal

phosphoric acid and on the other, the selective separation of uranium from wet-process phosphoric acid is concerned.

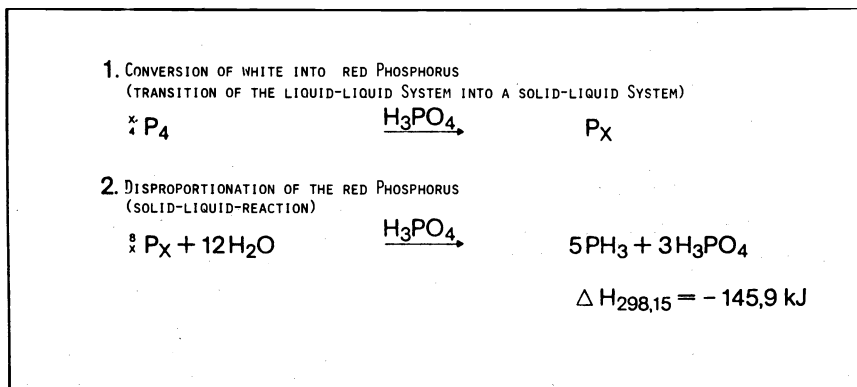


Figure 4. Disproportionation of elemental phosphorus in phosphoric acid

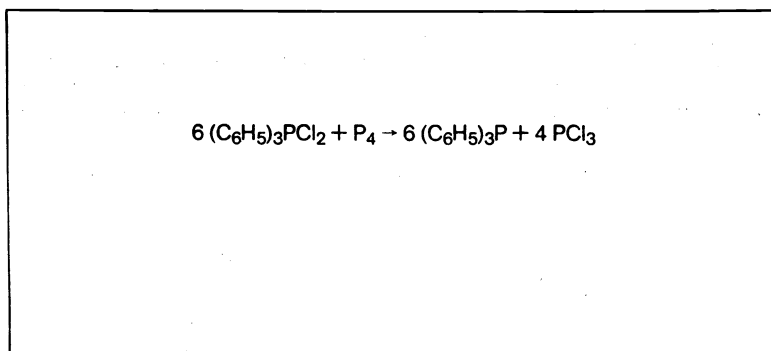


Figure 5: Reaction of Triphenyldichlorophosphorane with elemental phosphorus

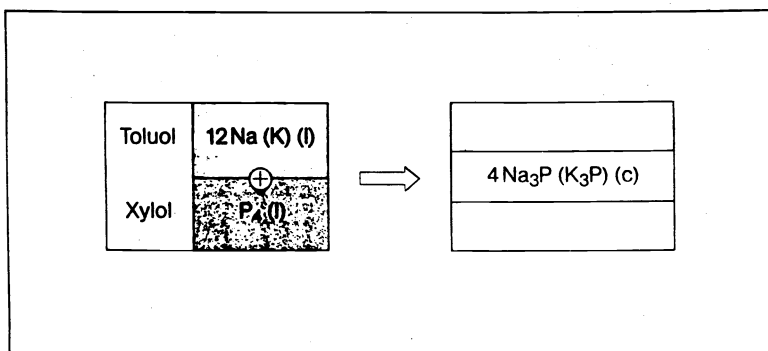


Figure 6. Preparation of Na_3P in a liquid-liquid-system

3.1 Purification of wet-process phosphoric acid

In the purification of wet-process phosphoric acid, liquid-liquid phase techniques are used for separation of the cationic impurities. This premises that solvents are available which possess high selectivity as regards solubility of the phosphoric acid vis-à-vis the metal cations which, in the form of dihydrogen phosphates, are retained in the aqueous phase by way of a kind of salting-out process.

3.1.1 Influence of the organic phase on process control

The following solvents have been used in production so far (table 3); depending on the particular conditions and circumstances, they have certain advantages and disadvantages.

In this way a high degree of purification can be dispensed with and only part of the acid used may be obtained in purified form, if the remainder containing all the cationic impurities is transferred to an adjacent fertilizer plant. This category includes processes with methyl isobutyl ketone (Ref. 8) and with diisopropyl ether (Ref. 9); in the latter case, as can be seen from fig. 7, the different solubilities of phosphoric acid at high and low temperatures are utilized for dissolution and re-separation of part of the phosphoric acid in pure form. The advantages conferred by the simplified liquid-liquid phase technique of these so-called splitting processes are partly offset by a number of disadvantages. Thus, for example, the entire crude phosphoric acid used - that is to say also that part which goes into fertilizer production later - has to be subjected to the relatively expensive pre-purification process for removal of anionic compounds such as arsenate and sulfate and also organic impurities.

When using water-miscible alcohols, for example, isopropanol, the entire alcohol has to be distilled from the phosphoric acid extract if the free phosphoric acid is to be isolated. Consequently these processes are more favourable if the pure phosphoric acid contained in the extract is salted out as sodium phosphate solution with the aid of sodium hydroxide, it being possible to separate and recycle the isopropanol as the upper phase (Ref.10). However, one is then forced to produce sodium phosphates which cannot be as widely used as free phosphoric acid.

With a number of extractants, for example, tributyl phosphate in kerosine, the distribution coefficient of phosphoric acid between the aqueous and the

organic phase is unfavourable so that either an elaborate extraction plant or, as in the splitting process, coupling with a fertilizer plant is required (Ref. 11).

| |
|--------------------------------------|
| ISOPROPANOL |
| N-BUTANOL |
| PENTANOLS (MIXED ISOMERES) |
| METHYLISOBUTYLKETONE |
| TRIBUTYLPHOSPHATE SOLVED IN KEROSENE |
| DIISOPROPYLETHER |

Table 3. Extraction purification of wet-process phosphoric acid (Solvents used in large scale production)

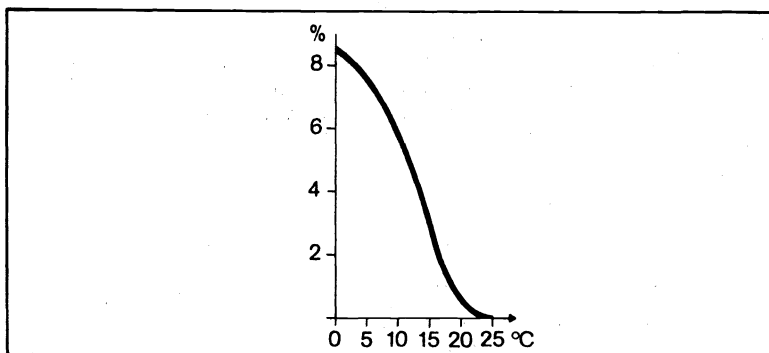


Figure 7. Solubility of H_3PO_4 in Diisopropylether
 H_3PO_4 50% P_2O_5 , Volume ether/
 Volume H_3PO_4 = 3,5)

Higher alcohols occupy a favourable intermediate position as regards process control and costs, for example, the mixture of isomeric pentanols from oxo synthesis (Ref. 12).

3.1.2 Process steps of wet-process phosphoric acid purification using liquid-liquid techniques

Nearly all extraction purification processes for wet-process phosphoric acid are based on the same flow sheet (fig. 8). In the first step of the process the pre-purified acid is transferred to the organic phase, with the main amount of cationic impurities remaining in the form of dihydrogen phosphates in the aqueous phase. If this process step is carried out in a liquid-liquid counter-current plant and free sulphuric acid is introduced at a suitable point in this separation step (fig. 9), a large proportion of the separated metal hydrogen phosphates is converted into hydrogen sulfates with liberation of further phosphoric acid, the extraction yield thus being increased to 95 % and more (fig. 10).

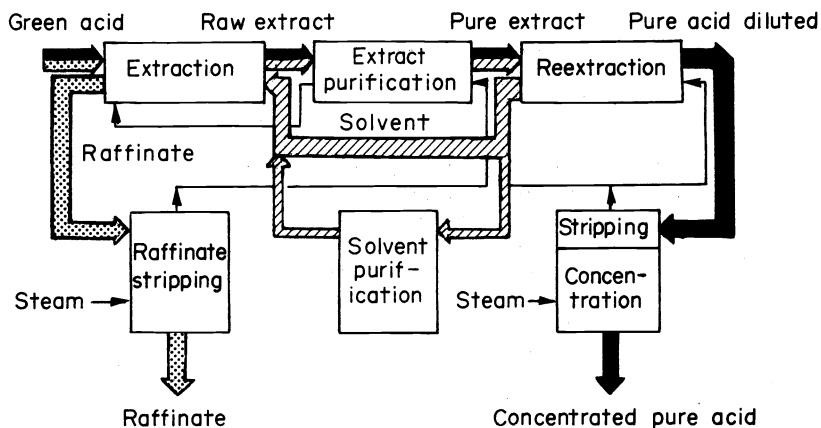


Figure 8. Extraction purification of wet-process phosphoric acid (general flow sheet)

The phosphoric acid extract from this first step still contains interfering residual cations in accordance with their distribution coefficients. Consequently an extract wash follows as the second step in which - again by way of a liquid-liquid counter-current extraction - the main proportion of these residual impurities is removed with water or pure phosphoric acid. The effectiveness of this step is demonstrated in fig. 11 with the aid of the ion concentration curve of iron as the reference element via 10 steps, again with amyl alcohol as the organic phase. The selectivity represented by the quotient in respect of the separation of iron(II) ions from phosphoric acid is about 1:20 under the chosen conditions.

In the third step finally, the phosphoric acid contained in the organic extract is converted into pure aqueous phosphoric acid, again in a liquid-liquid counter-current extraction process by the addition of water. Further process steps are: conversion of the raffinate of the first step into a product that can be taken to a waste dump, recovery of the solvent by stripping the main product and byproducts cleaning the circulating solvent (normally in a side-stream) and concentration of the re-extracted phosphoric acid to a content, for example, of 55 - 60 % P_2O_5 .

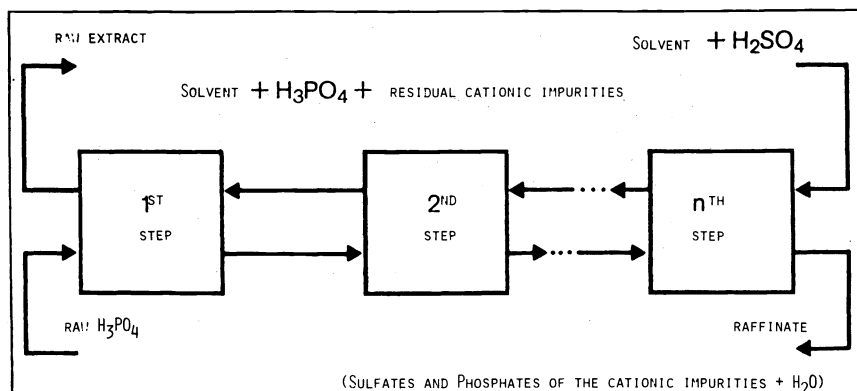


Figure 9. Extraction purification of wet-process phosphoric acid (Preparation of the extract)

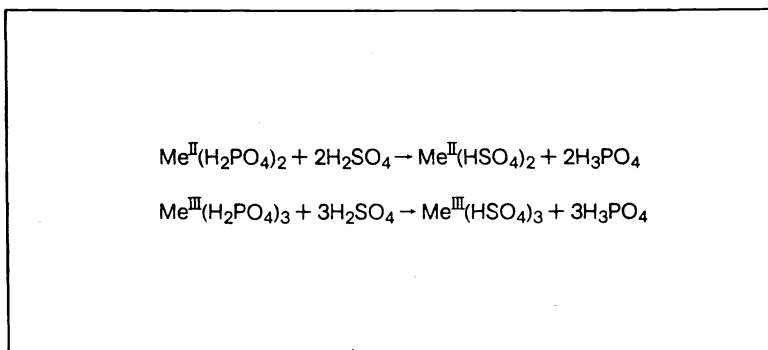


Figure 10. Extraction purification of wet-process phosphoric acid (Improvement of the H₃PO₄-yield addition of H₂SO₄)⁴

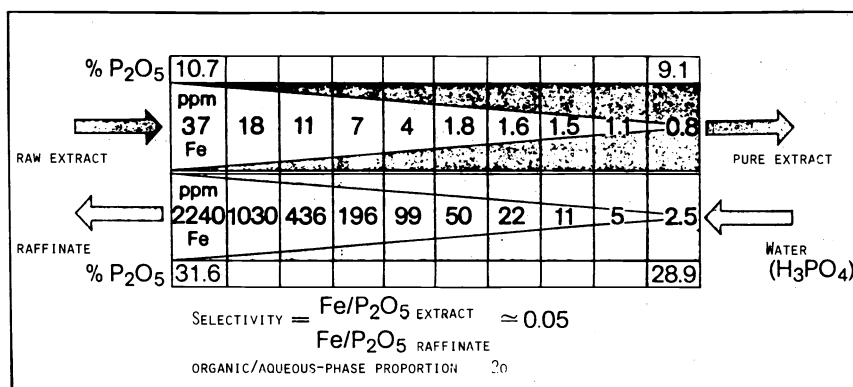


Figure 11. Extraction purification of wet-process phosphoric acid (Removal of Fe²⁺-ions by counter-current wash in the system C₅H₁₁OH-H₃PO₄-H₂O)

3.1.3 Technological developments and economic importance

The development of these extraction process for wet-process phosphoric acid had contributed considerably to the further development of liquid-liquid techniques generally during the last few years. Thus the system, because of the presence of cationic and various anionic impurities in the first process step, tends to form precipitations and encrustations which it has only been possible to prevent by special control of both liquid phases in newly developed mixer-settler units. Moreover, unusual ratios of the organic to the aqueous phase of 30 or even higher have to be employed in the second process step, which in turn necessitated further development of the various liquid-liquid phase techniques.

The capacities in the course of construction and in operation for extraction purification of wet-process phosphoric acid in western Europe listed in table 4 show that this technology has found wide acceptance on a production plant scale in the meantime (Ref. 14).

3.2 Uranium production from wet-process phosphoric acid

3.2.1 General

The second field of wet-process phosphoric acid technology, namely separation and production of uranium with the aid of liquid-liquid techniques, is on the threshold of wide technical application. The first production plants are currently being planned, built or put in operation.

According to the uranium content of the majority of phosphate ores, the phosphoric acids produced from them contain about 200-600 g uranium/tonne P₂O₅. Thus it will be possible in the long term to obtain several thousand tonnes of uranium per year throughout the world from this acid which is manufactured mainly for fertilizer production. After initial developments in the nineteen-fifties work in this field was discontinued; however, due to increasing uranium prices during the last few years, intensive work is now being resumed. In the meantime a large number of different processes for the liquid-liquid extraction of uranium from wet-process phosphoric acid has been developed, two groups of processes having come to the fore which evidently are the most suitable for industrial application. They differ mainly in respect of the solvent used in the first of two extraction cycles (Ref. 15, 16).

| | |
|---------------|---------|
| GERMANY | 105.000 |
| FRANCE | 100.000 |
| GREAT BRITAIN | 100.000 |
| BELGIUM | 50.000 |
| SPAIN | 10.000 |

Table 4. Extraction purification of wet-process phosphoric acid (Production capacity in western europe in t/a P_2O_5 in 1979, plants in operation and under construction)

3.2.2 Description of the processes

The most advanced processes are those of the group with trioctylphosphine oxide (TOPO) and diethylhexylphosphoric acid (DEPA) in kerosine as the organic phase. A few important data on the solvent systems are shown in table 5. In the TOPO-DEPA system the uranium must be present during extraction as the uranyl cation, i.e. in the hexavalent state. The second system consists of an approximately equimolar mixture of mono- and dioctylphenylphosphoric acid (OPAP), which are used dissolved in kerosine in the stated concentration. The phase ratio of organic phase to phosphoric acid is 1:4 here, instead of 1:2 as in the TOPO-DEPA system. In contrast to the TOPO-DEPA process the uranium has to be present in tetravalent form during extraction. Before extraction of the uranium the crude phosphoric acid has to be pretreated in

1. EXTRACTION IN FORM OF U-VI (DEPA-TOPO-PROCESS)

COMPOSITION OF THE ORGANIC PHASE:

SOLUTION OF TRIOCTYLPHOSPHINEOXIDE (0.125 MOL/L) AND
DIETHYLHEXYLPHOSPHORIC ACID (0.5 MOL/L)

PHASE PROPORTION ORGANIC/ H_3PO_4 (32% P_2O_5) $> 1 : 2$

2. EXTRACTION IN FORM OF U-IV (OPAP-PROCESS)

COMPOSITION OF THE ORGANIC PHASE.

SOLUTION OF MONOOCTYLPHENYLPHOSPHORIC ACID
DIOCTYLPHENYLPHOSPHORIC ACID (0.32 MOL/L)
IN KEROSENE

PHASE PROPORTION ORGANIC/ H_3PO_4 (32% P_2O_5) $\approx 1 : 4$

Table 5. Extraction of Uranium from wet-process phosphoric acid (Solvent Systems)

both cases similarly to the extraction purification referred to earlier, especially for removal of the partly considerable quantities of organic impurities which stem from the ore (fig. 12). As the uranium is preponderantly present in its tetravalent form in the crude acid, it (the uranium) has to be oxidized, for example, with sodium chlorate, before extraction in the first process. In the second system, conversely, if part of the uranium is present as U-VI, a reduction process has to be carried out with Fe(II)-containing phosphoric acid.

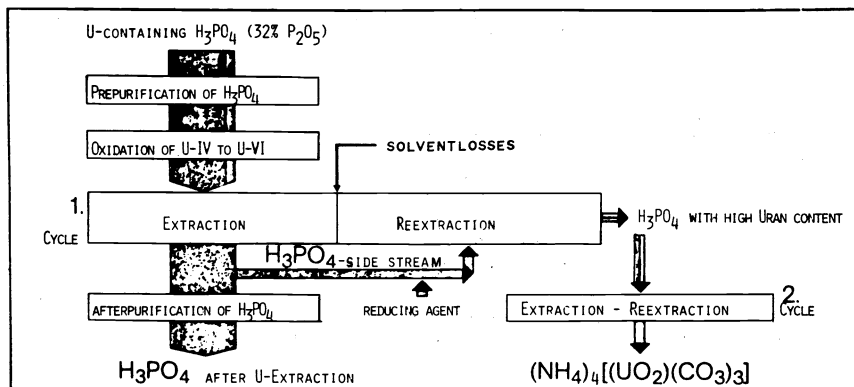


Figure 12. Extraction of Uranium from wet-process phosphoric acid (TOPO-DEPA-Process)

The products from the first extraction-re-extraction cycle are the H₃PO₄ main stream with depleted uranium content and a phosphoric acid part-stream enriched with tetravalent uranium.

In both systems, before the acid is transferred to the fertilizer production plant, this step is followed on the one hand by removal of the residual extractant from the H₃PO₄ main stream and on the other by further processing of the uranium-rich H₃PO₄ part-stream. This consists mainly of a second extraction cycle which operates by the "TOPO-DEPA" system in both cases.

In a French process the tetravalent uranium from the organic phase of the first cycle is separated directly with HF as pure UF₄ instead (Ref. 17). In the case of a second extraction cycle the uranium⁴ is finally precipitated as ammoniumuranyl carbonate and converted into U₃O₈.

In fig. 13 the first extraction cycle for the TOPO-DEPA process is shown in greater detail. The starting product is an acid very rich in uranium, containing 1700 ppm U. The concentration curve is shown both in the 4-step extraction section and in the two-step re-extraction section for the organic upper phase and the phosphoric acid bottom phase. In retransfer of the uranium from the organic to the acid phase a valency change U VI → U IV is required, which can be achieved via the iron(II) ions of the H₃PO₄ part-stream.

4. Examples from other substance classes

Liquid-liquid phase techniques are important not only in reactions of elemental phosphorus and in the wet-process phosphoric acid field, but also in a large number of other areas of industrial phosphorus chemistry.

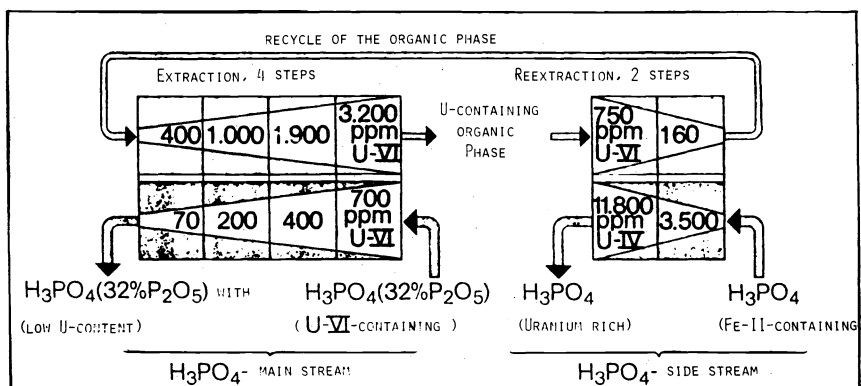


Figure 13. First extraction-reextraction-cycle of the TOPO-DEPA-Process (U-concentration of the original H_3PO_4 1700 ppm)

Thus dialkyldithiophosphoric acids, which are obtained in relatively impure form during the reaction of P_4S_{10} with alcohols, can be purified by first precipitating them as solid ammonium salts (fig. 14), for example, from a solution in toluene; these are then separated and brought into contact with excess phosphoric acid. Immiscible liquid phases form in the process, namely very pure dithiophosphoric acid as the upper phase and a useable ammoniumdihydrogen phosphate-containing phosphoric acid as the bottom phase (Ref. 18).

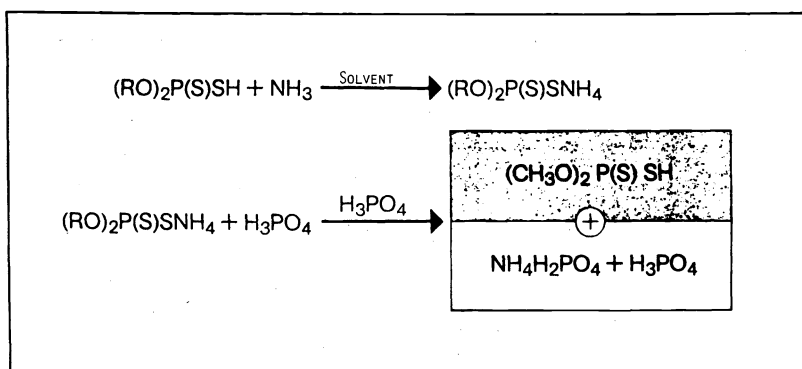


Figure 14. Purification of o,o Dialkyldithiophosphoric acid

Such a separation into two immiscible liquid phases can, for example, also be used for the separation of methylchlorophosphine and dimethylchlorophosphine (fig. 15). Dimethylchlorophosphine, because of its higher basicity, forms liquid adducts of a saltlike nature in the presence of HCl gas: these adducts do not mix with the free methylchlorophosphine which separates as the upper phase (Ref. 19).

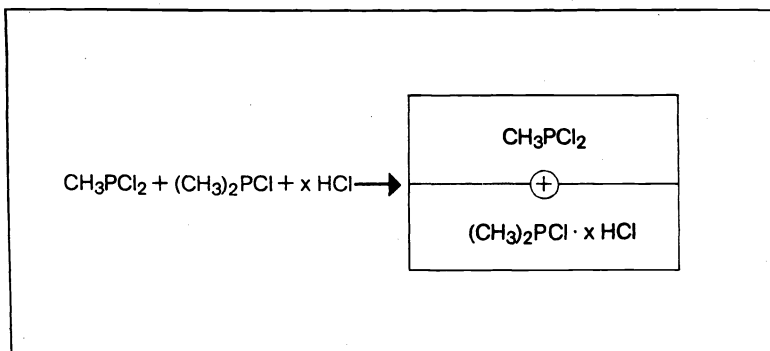


Figure 15. Separation of CH_3PCl_2 and $(\text{CH}_3)_2\text{PCl}$

A very interesting, relatively recent field in which phosphorus compounds in liquid-liquid systems are used, is that of phase transfer catalysis. Phosphonium bromides with longchain organyl groups have proved particularly suitable for this purpose (Ref. 20).

The small number of randomly selected examples could be considerably widened.

5. Conclusion

The use of a system consisting of two immiscible liquid phases that is predetermined by a certain substance system or reaction system, or with the aid of which, for example, it is intended to improve the course of a chemical reaction, or the separation of substances, normally results in an increase in the number of possibilities of variation in process control. Although the setup of the process technique becomes complicated as a result, additional attractive possibilities of improvements often present themselves, which can, for example, lead to a greater purity of the reaction products, increased product yields, savings in energy, isolation of valuable byproducts and numerous desirable effects. The wide application of many different liquid-liquid techniques is exemplary in industrial phosphorus chemistry, as was to be illustrated by means of the examples cited.

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