

# Quaternary ammonium salts of phosphines as ligands and their recycling by membrane techniques or phase separation. Part I: monophasic systems

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## Abstract

Quaternary ammonium salts of functionalized tertiary amines may serve as ligands for transition metal catalysts in hydroformylation reactions. Besides these properties they offer special advantages for the catalyst separation using phase separation or membrane techniques. © 1997 Elsevier Science S.A.

## 1. Introduction

Since the invention of the hydroformylation reaction in 1938 by Otto Roelen [1] a continuous development and change of catalysts have taken place. The original cobalt catalyst has been widely replaced by rhodium. In recent years, other metals like platinum or palladium [2] have emerged. The modification of the catalyst metals by ligands has been found to be a powerful tool for further improvements in activity and selectivity. Tertiary or ditertiary aryl or alkyl phosphines as special sterical rigid chelate ligands [3] or phosphites [4] can additionally enhance the activity and selectivity of the reaction and extend their scope.

Besides these modifications, a further development was mainly influenced and accelerated by changing the application phase of the catalysts. The introduction of aqueous two-phase catalysts to the hydroformylation of propylene on an economical scale in 1984 [5,6] triggered a spate of work on 'functionalized ligands' in order to prepare water-soluble [7–10] or other biphasic catalysts [11]. The functionalization was mostly affected by the introduction of sulfonic, carboxylic, or ammonium groups (and more recently by polyether groups) [12].

Normally, the sulfonic or carboxylic groups are connected with alkali or alkaline earth cations as counter-ions. If ammonium cations are used, the substituents of the nitrogen have an extreme influence on the properties of the functionalized ligands. Using trisulfonated triphenylphosphine (TPPTS) [13,14] a change in size and type of the cations leads to a total change in the physical properties. The whole system shifts from a water-soluble ('biphasic') to an insoluble ('mono-phasic') system by minor variations of the alkyl groups and substitution by hydrogen in the counter-ions (Fig. 1).

Both types of quaternary ammonium salts show different valid properties and can act as very useful ligands in homogeneous catalysis. Thus, water-insoluble ammonium salts show comparatively high reaction rates in 'mono-phasic' operation even for less reactive higher olefins. The complexes can be recycled after separation by a new membrane process [15]. Recycling of water-soluble ammonium salts is possible by simple phase separation. Their phase transfer characteristics enable also the conversion of higher olefins, which normally show a reduced reactivity due to restricted miscibility with the aqueous phase.

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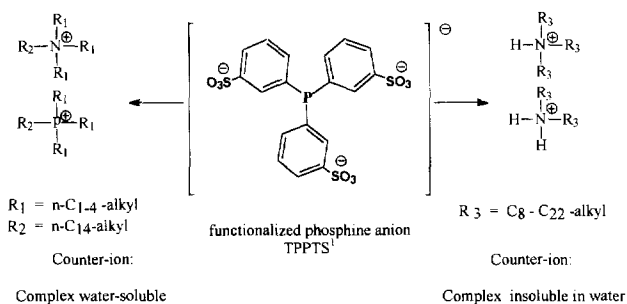


Fig. 1. Influence of cations on the properties of TPPTS salts triphenylphosphine trisulfonate.

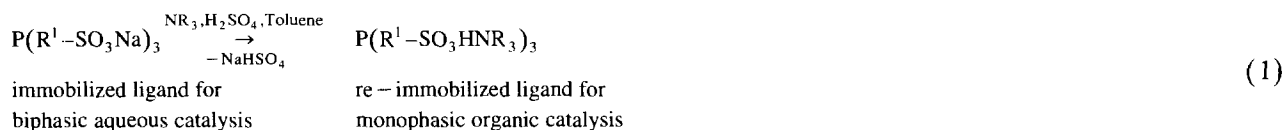
The chemistry and separation techniques of both types are out-lined in more detail mainly for the hydroformylation, mostly on the basis of TPPTS. Part II comprises biphasic catalytic systems [6].

## 2. Water-insoluble, re-immobilized lipophilic ligands and their separation by membrane technique

### 2.1. Chemistry of water-insoluble ammonium ligands

#### 2.1.1. Preparation

The water insoluble ammonium ligands are prepared from available water-soluble sodium salts according to Eq. (1).



By introducing different amines in solvents the sodium cations of the sulfonates can be exchanged in the presence of sulfuric acid. Sodium hydrogensulfate is formed as a by-product. Often the phase separation may be improved by the addition of lower alcohols such as isopropanol. According to Eq. (1) many variations are possible, such as different amines, functionalized phosphorus ligands, acids, solvents and preparation procedures.

The variation of monoamines was investigated in more detail. As can be inferred from Table 1 many different amines can be used.

It is possible to use primary and secondary amines as well as tertiary or multifunctional amines (entries 11–13 of Table 1). In all cases the P<sup>III</sup>-yield (transition into the organic phase) is sufficient. Upon increasing the molecular

Table 1  
Ligand preparation by variation of amines

Entry	Amine	Mol.-mass	Temp. (°C)	pH		Addition of <i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	P <sup>III</sup> content of phase (%)	
				start	end		lower aqueous	upper organic
1	Triisooctyl-amine	353.7	20		3.5	–	0.0	100
2	Methyl-di-tallowamine	513.6	60	7.3	3.5	+	0.8	100
3	Distearyl-amine	522.0	65	7.7	2.6	+	0.0	100
4	Methyl-di-stearylamine	536.0	60	9.0	3.6	+	—	93.9
5	Jeffamine M 600	600.0	20	10.0	1.8	–	1.6	88.6
6	Tricetylamine	690.3	20	7.5	3.5	–	6.6	98.7
7	Tristearyl-amine	740.8	60	5.7	1.0	–	0.6	87.0
8	Tri- <i>n</i> -octadecyl-amine	774.5	75	6.8	1.0	–	1.8	90.6
9	Trieicosyl-amine	858.6	75	6.8	0.0	–	1.1	95.5
10	Tridoeicosyl-amine	942.8	80	3.5	0.1	–	—	94.3
11	Jeffamine D 2000	2000	20	9.7	3.6	+	8.9	88.0
12	Jeffamine T 3000	3000	20	9.0	3.6	+	—	93.2
13	Jeffamine D 4000	4000	20	9.5	3.4	+	16.0	73.0

Solvent: 2.7 g toluene/g amine; source of phosphorus: TPPTS, 0.33 moles/mole amine; acid: sulfuric acid.

weight of the amines, the pH value is generally lower. Perhaps because of the large distance between the amine groups, the multifunctional amines do not tend to polymerize as do the lower amines (see below).

Normally, as outlined above, the 'triacidic acid' TPPTS was combined with 'monobasic amines' as bases. Dibasic amines such as 1,3-diaminopropane yield highly crosslinked polymeric materials, whereas other diamines like Thancat CD<sup>R</sup> ( $[(\text{CH}_3)_2\text{N}-\text{CH}_2-\text{CH}_2-\text{I}_2\text{O}]$ ) or 3,4,8,9-bis-dimethyl aminomethylene tricyclodecane result in the formation of very good water-soluble ligand salts.

Replacing the 'triacidic acid' TPPTS by the disulfonated TPPDS in the combination with TCD-diamine (tricyclodecane diamine) a salt partly soluble in toluene and soluble in THF was formed. The same is true with *N,N'*-dimethyl TCD-diamine instead of TCD-diamine. These salts may be useful in water-free (although bi-phasic) operation.

Sulfuric acid may be substituted by phosphoric acid. This could be of interest with respect to corrosion aspects. Under special circumstances even the olefin for the further catalysis may serve as a solvent itself. This concept was successfully realized with dicyclopentadiene (DCP).

In some cases, it is desirable and necessary to use phosphines with low basicity such as phosphites. In order to prepare ionic phosphites of the same structure as mentioned above, the preparation procedure [16] can be modified as outlined in Eqs. (2) and (3):



Z = Hal, OR

R<sup>1</sup> = C<sub>6</sub>H<sub>x</sub>, x = 6 - (n + m)

In a first step, sodium salts of hydroxysulfonic acids in aqueous solution are transferred to the corresponding ammonium salts by addition of amine, sulfuric acid, and an organic solvent, which is insoluble in water. The water is separated by phase separation and traces are removed by drying with Na<sub>2</sub>SO<sub>4</sub> and azeotropic distillation. In the second step, the dry solution of the ammonium salt of the hydroxysulfonic acid is reacted with PCl<sub>3</sub> or P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.

### 3. Separation and use of water-insoluble ammonium ligands in hydroformylation

Whereas on the one hand in hydroformylation with water-soluble ligands the catalyst can be separated easily after the reaction by simple phase separation, the conversion of higher olefins is normally poor and suffers from the reduced miscibility of both phases by restricted mass transfer. This can be overcome by different additional methods such as the use of water-soluble amphiphilic ammonium cations [17]. In addition, the very active and useful phosphite ligands must be excluded from the aqueous phase due to hydrolysis. On the other hand high conversion rates can be reached even with branched unreactive olefins using conventional homogeneous ligands in 'homophasic' operation, but separation of the catalysts may be a problem, especially with high-boiling substrates, which cannot be distilled.

By using water-insoluble ammonium ligands, the advantages of both catalyst systems (easy separation under mild reaction conditions and high conversion rate) can be combined while avoiding their disadvantages. Thus, hydroformylation with ionic phosphites (e.g. the triisooctylamine salt of *p*-sulfonated phosphorous acid triphenylester TPPpS-TIOA salt) was introduced by B. Fell and G. Papadogianakis [18] (Table 2).

Table 2  
Ligand testing by hydroformylation: ionic phosphites versus triphenylphosphine (TPP)

P/Rh ratio (mol/mol):	Triphenylphosphine (TPP)		TPPpS-TIOA salt <sup>a</sup>	
	40	80	40	80
Conversion (%)	81	83	71	70
l/b ratio <sup>b</sup>	72/28	72/28	83/17	87/13

Reaction conditions: olefinic feedstock: *n*-1-tetradecene; pressure: 50 bar; Rh concentration: 20 ppm; temp.: 125°C; reaction time: 3 h.; solvent: acetone.

<sup>a</sup>Triisooctylamine salts of *p*-sulfonated phosphorous acid triphenyl ester.

<sup>b</sup>l = linear; b = branched.

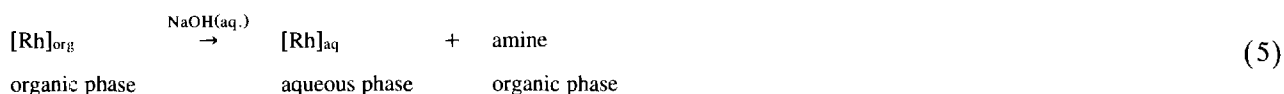
As compared with TPP the TPPpS–TIOA salt offers a significantly better ratio of linear/branched compounds (l/b ratio). For the separation and recycling of the water-insoluble ammonium salt ligands and Rh complexes, two different methods have proved their worth, i.e. the phase separation by pH change after reaction and the separation of the catalyst system by membrane filtration.

### 3.1. Phase separation by pH change after reaction

In this case the potential functionality of the ligands is applied to induce a phase transition of ligands and Rh complexes and subsequent phase-separation by a pH change after the reaction at room temperature. The principle is outlined in Eqs. (4) and (5).



and thus



By changing the pH value the water-insoluble ammonium salts are reconverted into water-soluble sodium sulfonates. The phosphine and the Rh catalyst are thus transferred to the aqueous phase. They can easily be separated from the organic product. A process scheme is outlined in Fig. 2: As can be seen from Fig. 2 the resulting aqueous catalyst phase can be further used in the biphasic catalyst system (such as the RCH/RP process, [6]) or may be re-immobilized in a regenerator with fresh  $\text{H}_2\text{SO}_4$ /amine for the next catalyst cycle. The amine content of the organic phase can be separated by distillation and recycled again by treatment with recycled sulfonated phosphine and sulfuric acid.

Using this procedure a variety of different olefinic compounds and structures (cycloaliphatic, internal, functionalized) have been tested with the triisooctylamine–TPPTS salt [19] (cf. Table 3).

Since fairly good results have been reached by hydroformylation of oleylic alcohol, the catalyst separation and recovery was investigated successfully in more detail on a pilot plant scale [20,21].

### 3.2. Separation of the catalyst by membrane filtration

The formation of salts according to Fig. 2 is environmentally disadvantageous. Thus, a separation of the catalyst system (Rh complexes as well as additional excess of stabilizing ligands) by membrane filtration ought to be the best way to overcome this and other disadvantages.

#### 3.2.1. State of the art

The first patents on membrane filtration of organic soluble Group VIII metal catalysts from the crude reaction product of a transition metal catalyzed hydroformylation in organic solution emerged from British Petroleum in 1968–1970 [22–25]. They describe the separation of organometallic complex compounds such as  $\text{RhCO}(\text{PBU}_3)_3$  by means of membranes while allowing small organic molecules (including excess of ligands) to permeate under reverse osmosis (RO) conditions (high pressures [50–100 bar], low flow rates [1–4 l m<sup>-2</sup> h<sup>-1</sup>], and a solute rejection of about 78–94%). Similar results were reported in 1973 by Monsanto [26] or by Gosser [27–29]. Due to the

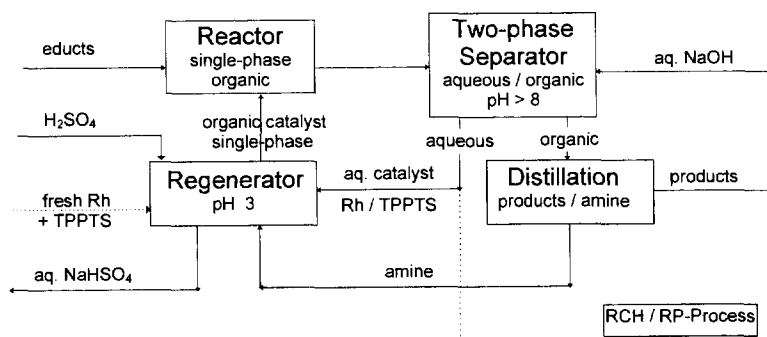


Fig. 2. Catalyst recycling by pH-induced phase separation.

Table 3  
Hydroformylations with trisooctylamine–TPPTS salts (variation of alkenes)

Alkene	Rh (ppm)	Ratio P <sup>III</sup> /Rh <sup>a</sup> (mole/mole)	Pressure (bar)	Conversion (%)	l/b ratio <sup>b</sup>	Rh and ligand recovery by cation interchange <sup>c</sup> (%)
Cyclohexene	9	120	270	100	—	31
Dimersol <sup>d</sup>	9	124	270	81	—	32
Diisobutene	26	36	270	99	—	42
Dicyclopentadiene	53	60	270	100	—	79
1-Hexene <sup>e</sup>	10	100	25	77	64/36	74
Limonene	132	120	270	98	—	93
1-Decene	44	118	270	99	65/35	100
Oleyl alcohol <sup>f</sup>	44	70	270	98	—	92
Methyl acrylate <sup>g</sup>	100	60	270	100	96/4 <sup>h</sup>	87

Constant reaction conditions: Temp.: 130°C; Reaction time: 6 h.

<sup>a</sup> Before reaction.

<sup>b</sup> Linear/branched.

<sup>c</sup> Extraction with aqueous NaOH, phase separation and subsequent re-extraction with toluene-amine and H<sub>2</sub>SO<sub>4</sub>.

<sup>d</sup> Product from dimerization of *n*-butenes, trademark IFP.

<sup>e</sup> Reaction time 2.5 h.

<sup>f</sup> HD-ocenol 90/95<sup>®</sup> of Henkel Corp.

<sup>g</sup> Reaction time 2 h.

<sup>h</sup> Ratio of  $\alpha$ -formylpropionate to  $\beta$ -formylpropionate.

permeability of the ligands, the ligand to metal ratio is continuously changing, and real recycling of the whole catalyst system is impossible.

A general breakthrough was achieved in 1986 by E. Bayer [30] when he changed from RO to ultrafiltration (UF) at lower pressures (2 bar), higher flow rates (20 l m<sup>-2</sup> h<sup>-1</sup>), and a satisfying metal retention. He used anchored catalysts on 'mobil supports', such as soluble macromolecularly P-functionalized polystyrene with a high molecular mass of about 10.000. This system suffers from fundamental disadvantages: because of the extremely high molecular mass of the ligand, it is impossible to realize the high P/Rh ratio which is needed to stabilize the active catalyst complex and to ensure a long lifetime. In addition, the absence of an excess of free ligands makes a catalyst more sensitive to traces of oxygen and other poisons in technical operation.

Other relevant work with hydroformylation products and their membrane separation has been reported by Halligudi et al. [31] and by Exxon researchers [32] under modified conditions and using newly developed membranes.

### 3.2.2. Recent developments

3.2.2.1. *Basics.* The challenge to enable a good retention for both, metal complexes and free ligands requires

1. the development of new membranes resistant to organic liquids with a narrow cut-off in a molecular mass (mm) range between 1.000 and 10.000
2. an oxo raw material with a high process development and market potential, and
3. the choice and development of appropriate ligands (mm 1.000–10.000).

At the beginning in 1987, the first requirement was not given, because experiments with commercially available membranes showed insufficient stability to organic products, especially against oxo products. Since 1988 a new polyamide membrane (UF-PA-5 from Hoechst AG) with outstanding properties, which met all requirements, was available [33].

The second requirement was met with the decision to use tricyclodecane dialdehyde ('TCD dial') from the hydroformylation of dicyclopentadiene (DCP). TCD dial is the starting product for TCD diamine, which is a specialty chemical used as a curing agent for epoxy resins (Eq. (6), [34]).



DCP is normally hydroformylated using unmodified Rh catalysts yielding high TCD dial contents under inconvenient Rh recycling conditions. It was found that on hydroformylating DCP an ammonium salt modified phosphine Rh catalyst can also be used (cf. Table 3).

The third requirement was achieved by the use of the 'reimmobilized catalysts' which enable a fine-tuning of the size of the ligands by variation of amines due to their modular ionic structure. Since the development of effective and efficient ligands is costly and exceeds the value of the transition metals it becomes necessary to separate and recycle the ligands, too. Moreover, the structure of the re-immobilizing ligands makes it possible to remove phosphine oxides and other poisons during economical operation by a simple washing procedure. In the final treatment of the ligand, normally all of the ligand is lost, whereas in the case of ionic ligands the ammonium backbone can be reused.

First results in membrane filtration with a polyamide membrane and a conventional Rh/TPP catalysts were unsatisfactory, because of the low mM < 1000 of the Rh complex itself. Only the use of the re-immobilized catalyst with a higher molecular mass (> 3.000) showed an encouraging Rh retention of 96% as compared to 50% with TPP [35].

**3.2.2.2. Mutual optimization of hydroformylation and membrane filtration step.** This mutual optimization could be achieved via variation of amines and the P/Rh ratio as well as by introduction of chelating ligands. A variety of amines was tested with TCD dial with respect to conversion and selectivity to dialdehyde as well as to the separation figures in the subsequent membrane separation step. Table 4 shows some results.

With an increasing molecular mass of the amines, a lower yield of dialdehyde was observed. Jeffamines, which are polyether based primary amines, showed significantly poorer selectivities than secondary or tertiary ones. Some medium sized amines tend to precipitate below 40°C which offers the possibility of catalyst separation by cooling and filtration. In the membrane separation step the increasing molecular masses of the amines lead to improved retention of rhodium, phosphorus ligand, and of the amines. To understand the membrane figures it must be born in mind that retention and permeate flux are generally a function of the amount of permeate. The higher the amount of the permeate, the lower its flux and retention figures. This is due to the higher concentration of compounds within the retentate (osmotic pressure). The best results show catalyst systems with overall high values for concentration (amount of permeate), flux, and retention. Distearyl amine fits these requirements. In addition it is cheap and available. So, this amine was used as standard and in subsequent replication experiments.

In Table 4 the retention of amines is stated, too. This is due to the fact that in the course of our investigations we always found traces of amine in the permeate. This is a result of a very low temperature-dependent dissociation of the ammonium salts into amine and free acid during the hydroformylation reaction according to Eq. (7).



In order to stabilize the ammonium salts it was necessary to allow some amount of free amines. With respect to this additional requirement, an ideal system must have the same good retention for amines as well as for the rhodium and

Table 4  
Hydroformylation of dicyclopentadiene and membrane separation of the catalyst system (variation of amines)

Amine	Mass mol.	Conv. (%)	Selectivity dialdehyde monenal	ratio <sup>a</sup> P <sup>III</sup> /Rh	pH value after reaction	Permeate amount (% of input)	Permeate flux <sup>c</sup> (l m <sup>-2</sup> h <sup>-1</sup> )	Retention (%) of		
								[Rh]	Ligand [P]	Amine [N]
Trisooctyl-amine	353.7	99.9	99/1	74	—	5–15	65–64	89.3	69.8	16.5
Methyl-di-tallowamine	513.6	99.6	92/8	41	4.0	11	71	91.9	95.0	76.4
Distearyl-amine	522.0	98.4	97/3	72	4.0	66	67–61	97.5	96.1	78.3
Methyl-di-stearylamine	536.0	99.4	95/5	63	4.3	5–10	82–77	97.1	94.3	
Jeffamine M 600	600.0	98.8	40/60	51	3.3	23	9	99.7	98.7	63.9
Tricetylamine	690.3	98.7	96/4	78	—	22	44	95.0	90.0	73.3
Tri- <i>n</i> -octadecyl-amine	774.5	98.5	91/9	84	—	53	68–49	93.0	87.0	88.7
Tricosyl-amine <sup>b</sup>	858.6	99.0	95/5	103	—	22	57–59	98.9	95.9	88.3
Tridocosyl-amine <sup>b</sup>	942.8	99.7	90/10	—	—	48.8	44–29	96.5	94.7	81.9
Jeffamine D 2000	2000	98.1	69/31	7.6	4.0	29	23–22	99.5	89.4	93.9
Jeffamine T 3000	3000	98.4	63/37	3.9	6.2	56	45–31	99.7	97.7	91.4

Hydroformylation conditions: solvent: about 50% toluene; phosphorus source: TPPTS, 0.33 mol/mol amine; pressure: 270 bar; Rh concentration: 60 ppm; P/Rh ratio: 100; reaction temp: 130°C; reaction time: 4 h. Membrane separation conditions: feed: reaction product of hydroformylation of dicyclopentadiene; solvent: about 50% toluene; membrane: UF-PA-5/PET 100 from Hoechst AG; overflow: ~ 200 l/h; separation temp.: 40°C; pretreatment of membranes in water at 80°C for 10 min; transmembrane pressure: 10 bar.

<sup>a</sup>After reaction.

<sup>b</sup>Precipitation of the ligand below 40°C.

<sup>c</sup>Initial-final value.

Table 5  
Recycling series with a Rh-distearylamine–TPPTS catalyst and a high P/Rh ratio

Hydroformylation			Membrane filtration					
Reaction time (h)	Temp. (°C)	No. of recycle	amount of permeate (% of input)		retention (% of input)		flowrate (l m <sup>-2</sup> h <sup>-1</sup> ) <sup>a</sup>	
			1st stage	2nd stage	Rh	P (total)	1st stage	2nd stage
2	125	0	87	86	95.96	89.3	103–10	136–51
2	125	1	85	94	99.23	92.7	97–16	115–40
2	125	2	85	96	99.71	99.3	92–17	82–29
2	125	3	88	93	98.85	99.2	82–15	75–24
2	125	4	84	94	99.30	99.4	76–17	68–28
2.3	125	5	82	90	99.57	98.9	72–17	56–15
2.5	127	6	83	95	98.61	99.0	67–13	66–18
2	128	7	84	93	99.52	97.2	67–12	89–30
2	126	8	83	94	99.09	96.7	63–10	74–16
2	128	9	83	94	99.07	97.6	58–10	76–22
2.5	125	10	81	93	98.80	98.2	56–12	62–21

Hydroformylation conditions: propylene; pressure: 270 bar; Rh concentration: 80 ppm; P/Rh ratio: 100; conversion: > 95%; l/b ratio, 63/37. Membrane separation conditions: feed, butyraldehyde; membrane type: UF-PA-5/PET 100 from Hoechst AG; pressure: 15 bar; reaction temperature: 20°C; residual content of amine in permeate: av. 5.1 ppm.<sup>a</sup>Initial–final value.

the ligands. In this light the choice of distearyl amine could only be regarded as a good compromise between hydroformylation and membrane separation figures. Thus, further optimization work was done by hydroformylation of DCP or propylene, respectively, with the Rh-distearyl amine/TPPTS catalyst system.

Test runs with low P/Rh ratios and Rh concentrations while hydroformylating DCP showed excellent membrane separation figures but decreasing activity figures. This failure in the optimization approach of the hydroformylation and membrane separation step without regard to long-term stability again underlines a basic problem in catalyst development, the coincidental consideration of different contradictory circumstances.

A second series with a high P/Rh ratio of 100 was performed with the same catalyst system and butyraldehyde from the hydroformylation of propylene as feed (cf. Table 5). This replication series shows overall excellent results in the hydroformylation as well as in the membrane separation step. With a high P/Rh ratio no deactivation was observed. The activity of the catalyst remained sufficient and high amounts of permeate with stable flow rates of 10 to 12 l m<sup>-2</sup> h<sup>-1</sup> in the critical first stage could be achieved. Obviously, traces of amine in the system catalyze some formation of high boiling components.

Whereas on the one hand, a sufficiently high excess of ligands is required for the stabilization of the catalyst system, on the other hand, this high excess of ligands leads to limitations, which depend on the physical properties of such excess ('salt effect' of the ligands). Thus, in turn reduces the permeate flow rate and the degree of thickening of the membrane filtration.

These contradictory effects with monodentate phosphines may be overcome by the use of bidentate ligands. Chelating ligands as strong complexing agents generally don't need a high excess of free uncomplexed ligands for the stabilization of the active catalyst complex. They make it possible to perform the hydroformylation reaction at a lower P/Rh ratio. Table 6 shows first results with an ammonium salt of simple functionalized chelating ligands, the distearyl amine/1,3-bis-disulfonato phenylphosphino propane salt and butyraldehyde from the hydroformylation of

Table 6  
Replication series with Rh-distearylamine-1,3-bis-disulfonatophenyl phosphinopropane catalyst

Hydroformylation		Membrane filtration					
Conversion (%)	l/b ratio	No. of recycle	Retention (%)			Flow rate (l m <sup>-2</sup> h <sup>-1</sup> ) <sup>b</sup>	
			Rh	P (total)	N	1st stage	2nd stage
93.9	55/45	0	96.4	80.9	60.3	92–59	119–75
85.4	56/44	1	97.7	88.8	58.7	82–54 <sup>a</sup>	112–72
88.6	55/45	2					

Hydroformylation conditions: feed: propylene; 270 bar; 125°C; P/Rh ratio: 2; reaction time: 2 h; Rh concentration: 20 ppm; Membrane separation conditions: feed: butyraldehyde; membrane type: UF-PA-5/PET 100 from Hoechst AG; pressure: 15 bar; temp: 40°C; amount of permeate: 1st stage: 91–84%; 2nd stage: 95–92%.

<sup>a</sup>Addition of 0.4 mmol P<sup>III</sup> of ligand to the permeate of the first stage.

<sup>b</sup>Initial–final value.

propylene as feed. Generally, retention figures were somewhat poorer, but very high flow rates could be achieved. On the basis of these results, an increase of the flow-rate from 10–12 up to 30–50 l m<sup>-2</sup> h<sup>-1</sup> by a factor of 3–4 could be reached. Additionally, the amount of ligand could be reduced by a factor of 50 and the Rh concentration by a factor of 2–3.

### 3.2.2.3. Membrane techniques on a pilot plant scale. [36]

Finally, the separation of the Rh-distearylamine/TPPTS catalyst system by membranes was successfully tested on pilot plant scale with crude aldehyde from the hydroformylation of DCP. The unit was continuously operated over a period of 12 weeks. No decrease of permeate flux and catalyst activity was observed. In contrast to lab-scale results, the Rh concentration must be increased to 100 ppm in order to get a selectivity > 90% of dialdehyde. The recirculation rate of Rh was established at 99.2% and of the ligand up to 98%. The permeate flux was roughly 10 l m<sup>-2</sup> h<sup>-1</sup>. Most of the loss of ligand was due to traces of oxygen.

## 4. Separation of phosphine oxides and other degradation products

The special functionality of the ionic phosphines enables a continuous catalyst make-up. Phosphine oxides and other degradation products can be separated from phosphine oxide by simple extraction with a diluted aqueous sodium hydroxide solution. The concentration of the aqueous sodium hydroxide and the extraction temperature have a tremendous influence on the extraction figures. At low concentrations (0.01%) only the water-soluble sodium phosphine oxides and some sodium salt of benzenesulfonic acid (a degradation product of TPPTS) are extracted into the aqueous phase selectively, whereas at higher concentrations up from 0.05% and more some of the phosphine is discharged, too. This simple selective separation of phosphine oxides and degradation products in continuous operation can enhance the lifetime of the catalyst system. The amount of aqueous NaOH can be adjusted to the degradation rate, which is much lower than the extraction rate. An adequate amount of NaTPPTS may be added together with the aqueous NaOH for generation of new ammonium salts from the amine, which will be formed by this procedure (see Eqs. (4) and (5)).

If higher concentrations of aqueous sodium hydroxide (15%) are used, all of the re-immobilized ligands and the rhodium complex can be extracted into the aqueous phase. This can thus be submitted to the oxidative treatment for Rh recovery according to refs. [37–39]. In this way, 92–95% of the Rh content may be recovered. The amine content of the organic phase was used again by treatment with fresh sulfonated phosphine and sulfuric acid. In the subsequent hydroformylation the same figures were actually observed.

## 5. Discussion of results and further development

Tailor-made quaternary ammonium salts of functionalized tertiary phosphines have been successfully used as ligands in the hydroformylation and the subsequent separation of the homogeneous catalysts by membranes. The ratio of the molecular weights of the ligands and the reaction products has been optimized in such a way that optimal results could be reached in the hydroformylation as well as in the membrane step. Both, Rh complexes and ligands were separated and recycled. The concept has been successfully proven with a simple modified tert. phosphine on pilot plant scale. Further improvements should be possible with chelate ligands. On the other hand it was found out that despite the low P/Rh ratio with chelate ligands, obviously the steric crowding makes them extremely sensitive to different effects. So only simple chelate ligands work fairly well with the simple olefin propylene and its hydroformylation products. In order to overcome this disadvantage, the number of the sulfonate groups should be reduced and located at greater distance from the metal center of the catalyst complex.

Due to their salt-like structure, the quaternary ammonium salts enable a selective continuous separation of phosphine oxides and degradation products during the hydroformylation reaction and thus a prolongation of catalyst lifetime. The amine backbone can be re-used. The final recovery of valuable metal, anions, or cations is possible by simple neutralization reactions.

Additionally, other types of ligands could be used which have the right molecular weight to enable sufficient retention in the subsequent membrane separation step.



## 6. Experimental section

### 6.1. General procedures

Preparations were manipulated in an inert atmosphere using Schlenk techniques. Solvents were freed from oxygen by bubbling nitrogen through the dip pipe for 2 h in presence of the aqueous TPPTS solution because it was found that this was the most effective method of removing and excluding oxygen from the organic products. TPPTS and TPPDS were prepared according to Ruhrchemie techniques [14]. Rh containing catalyst solutions were purged 5 times while stirring with syngas at 270 bar and subsequent expansion at rt prior to hydroformylation. Hydroformylations were performed according to standard procedures in a 5 l stirring autoclave with a dip pipe for gas inlet and products as well as a valve for off-gas. The transfer of catalyst solutions followed Schlenk technique as well.

### 6.2. Preparation of distearyl ammonium-TPPTS salt (Table 1)

To a three-necked stirring flask with reflux condenser, nitrogen inlet, and a valve at the bottom 531.5 g distearylamine were stirred into 1541 g toluene at 65°C until the amine dissolved. After this a aqueous solution of 655.0 grams of sodium tris(phenylphosphine) trisulfonate (514 mmol, residual content of phenyl disulfonatophenyl phosphine disodium salt, 41.9 mmol) was added. The pH value was 7.7. By addition of 233 ml diluted sulfuric acid (20%) within 1 h a pH value of 2.6 was reached. Stirring was continued for 2.5 hours. For better phase separation isopropanol (440.1 g) was added. The lower phase (715 g), which contains only small amounts of phosphorus<sup>III</sup> was discharged. The upper phase (2685.9 g, 126.0 mmol P<sup>III</sup>/kg) contained the re-immobilized TPPTS amine salt. It was further characterized by P analysis and after degradation (aqueous NaOH) by the HPLC analysis of the sodium salts and N analysis of the released amine.

### 6.3. Preparation of the distearyl ammonium salt of sulfonated 1,3-bis-diphenylphosphino propane

1,3-bis-diphenylphosphino propane was sulfonated with 25% oleum (P:SO<sub>3</sub> = 1:25) 72 h at rt. The resulting mixture was hydrolyzed by addition of cold water. The P<sup>III</sup> concentration of the diluted mixture amounted to 42 mmol/kg. According to HPLC analysis the mixture consists of 12% tetrasulfonated and 70% trisulfonated compounds and the corresponding oxides. 460.6 g of this mixture were placed in a three-necked stirring flask with reflux condenser, nitrogen inlet, and a valve at the bottom. A solution of 96.6 g distearylamine in 386 g toluene was added and the mixture was stirred at 50°C for 1 h. After reaction the lower, sulfuric acid containing aqueous phase was separated and discharged. By addition of an aqueous sodium hydroxide solution (5%) the pH value of the upper phase was adjusted to 2.6 at 45°C. The mixture was further stirred for 20 mins. Addition of 129 g toluene improved the phase separation within 30 min. The upper phase contained 662.9 g of a toluene solution of the distearyl amine salt of the 1,3-bis-disulfonato phenylphosphino propane. The P<sup>III</sup> transition into the organic phase was determined to correspond to 78.9% of the input.

### 6.4. General procedure of membrane filtration

Fig. 3 shows a simplified flowscheme of the lab-scale membrane unit. All valves are omitted for clearance. All connections to environmental atmosphere are sealed by silicon oil filled traps with an excess of nitrogen pressure. In order to prevent P<sup>III</sup> oxidation it has been found to be essential to use metal connection, even for the supply pipes for nitrogen, because oxygen diffusion through flexible rubber or teflon hoses was greater than expected.

The unit consisted of an inner and outer feed and/or retentate circuit and optionally an permeate recycling circuit. In the outer cycle the feed (hydroformylation reaction product) was pumped from the retentate flask through changeable fine filters to the membrane cell and from there via an overflow valve back to the retentate flask with a flow rate of about 10 l/h at a pressure of 145 to 290 psig (10–20 bar) by means of the membrane pump. In the inner cycle a part of the retentate product of the outer cycle was separated directly after the membrane cell and accelerated by a gear pump to 400 l/h back to the membrane cell. The permeate recycling circuit was used in the starting-up procedure until reaching steady-state conditions of the whole system.

The membrane unit consisted of a radial flow high pressure filtration cell made of stainless steel AISI 316 Ti (german stainless steel 1.4571) with Viton (or Teflon) sealing with a diameter of 76 mm and connections with fittings for 6 mm tube (Type DH-120 from Berghof Labor- and Automatisierungstechnik GmbH, Enigen, Germany). The membrane cell and some lines were wrapped with electric heater band for temperature regulation. The membrane (polyamide PA 5 from Hoechst AG) was delivered in welded plastic sheets and impregnated with glycerol/formal-

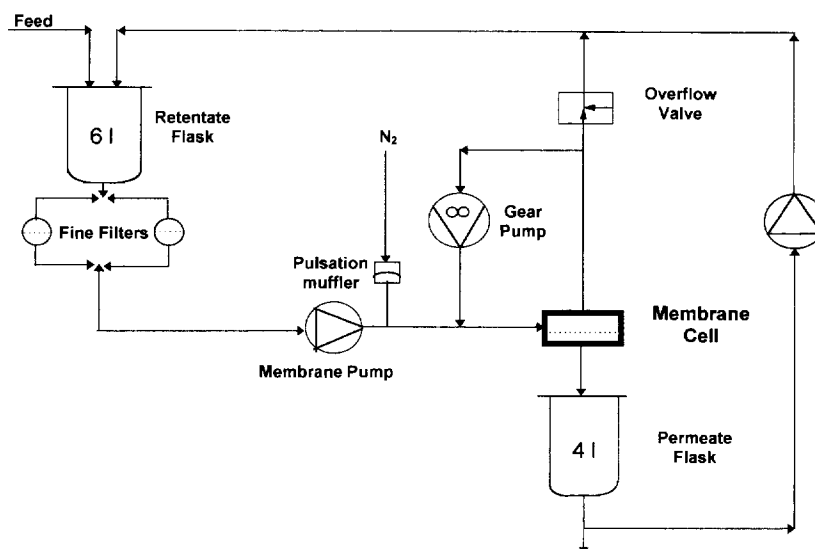


Fig. 3. Lab-scale membrane unit.

dehyde. The membranes were washed with water and pretreated (conditioned) at 80–100°C with water for 10 min. Thus, the membranes achieved the best properties. Then the membrane was subsequently washed with *i*-propanol and toluene. After this, the membrane was immediately incorporated into the cell according to the instructions for use by Berghof. Otherwise, the membrane surface suffers irreparable damage by drying. The best material for sealing rings is teflon.

Before starting the membrane unit, it was purged for 2 h with nitrogen. Leakproofing of the unit was done with toluene. For this purpose the retentate flask was filled with toluene and the membrane pump was started. The overflow valve was put out of function by using a bypass (not incorporated in Fig. 3). After 5 min the bypass was closed and the desired pressure was adjusted by the overflow valve. At the same time the pulsation muffer was adjusted with corresponding N<sub>2</sub> pressure. All connections of the unit were tested for leaks. After this the toluene was discharged by drain valves at the bottom of the membrane and gear pump (not incorporated in Fig. 3). Residual amounts of solvent are discharged by the bleed valve of the gear pump with N<sub>2</sub> pressure (not shown in Fig. 3). Then the retentate flask was filled with hydroformylation product by means of the Schlenk technique with nitrogen. If desired, additional solvent was added at this stage. The membrane pump and heating was started and the mixture was circulated for 2 h without pressure for mixing. The desired pressure was adjusted by means of the overflow valve. Additionally, the gear pump was started. The permeate was recycled using the permeate recycling circuit until the required temperature was reached.

After reaching set temperature the permeate recycle was stopped and the permeate was collected in the permeate flask. The amount was measured as a balance. The flow rate (l m<sup>-2</sup> h<sup>-1</sup>) was determined by a small scale receiving flask between membrane cell and permeate flask (not shown in Fig. 3). Depending on product and catalyst, 75–90% of permeate, relative to the feed was collected. Permeate and retentate were submitted to analysis for Rh, P, P<sup>III</sup>, and N in order to determine retention figures. Normally, the retentate was transferred to a three-necked flask for storage and the permeate was membrane filtrated in a second stage. The retentate of the second stage was unified with the product of the first stage and normally re-used as catalyst feed in a further hydroformylation run.

### 6.5. Pilot-plant tests

The pilot plant consisted of a 17 l tubular flow oxo-reactor and a two-stage membrane unit, which was directly connected to the reactor. The membrane surface area of the first stage was 1.4 m<sup>2</sup> and for the second step 0.2 m<sup>2</sup>. Standard plate modules from Dow (Type DDS 30-4.5) were used. The viscosity of the mixture was adjusted by addition of approx. 50% of toluene. The conditions of hydroformylation and membrane separation were the same as outlined in the replication series with the exception that a high P/Rh ratio of 100 was used throughout and the reaction temperature was raised to 130°C. The concentrate of Rh complexes and ligand (retentates) diluted in aldehydes, solvent and some high-boilers were recycled to the reactor.

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