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## Recovery of Styrene With Silver Fluoborate Solutions

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## RECOVERY OF STYRENE WITH SILVER FLUOBORATE SOLUTIONS

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England.

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## I. Introduction

The ability of metallic salts to form complexes with olefins and aromatic hydrocarbons has been known for a long time<sup>(1)</sup>.

With silver salts the reaction is truly reversible and the hydrocarbons can be recovered by the application of a thermal swing. In the early sixties data were released relating to the use of aqueous solutions of silver fluoborate and fluosilicate to form complexes with olefins<sup>(2)</sup>. These particular silver salts are highly soluble in water and can be used in concentrated aqueous solutions which are therefore capable of absorbing large quantities of olefin. These salts are also capable of absorbing a high proportion of olefin per unit weight of silver. Further, aqueous solutions of silver fluoborate, containing 850 g.Ag./l., are mobile below 0°C. With this knowledge Imperial Chemical Industries Limited set out to investigate the use of aqueous silver fluoborate to recover styrene from admixture with other C<sub>8</sub> aromatics.

In certain instances derived and experimentally obtained data were used. Where assumptions had to be made they were based on sound physical chemistry concepts and are therefore of general interest.

## II. Background Information

Apart from the self evident advantage of being able to separate pure ethylbenzene for styrene manufacture from  $C_8$  aromatics, it is found that many processes for para-xylene production operate more efficiently with a feedstock which contains little ethylbenzene. A schematic outline of a typical para-xylene process is given in Figure 1. Fresh feed, plus topped and tailed product from the isomerisation reactor is crystallised and the solid separated in rotary filters. After melting, the stream now containing about 70% para-xylene is recrystallised, and the final purification to give >99% para-xylene can be carried out by, for example, centrifugation. The mother liquor from the rotary filters is returned to the isomerisation reactor. In the reaction stage thermodynamic equilibrium is restored amongst the isomeric xylenes, the para-xylene level being increased to about 20%. The small amounts of benzene, toluene,  $C_9$ , and  $C_{10}$  aromatics produced by disproportionation reactions at the isomerisation stage are removed in the topping and tailing stills. At the time the work with aqueous silver fluoborate was started I.C.I. was paying a premium for a  $C_8$  aromatic feedstock low in ethylbenzene content (>5%). Feedstocks containing 20% ethylbenzene were more widely available. In order that the latter feedstocks might be used it is desirable that the ethylbenzene can be profitably utilised, for example, as a source of styrene. In the past dehydrogenation of ethylbenzene in mixed xylenes had not proved attractive because of the difficulty of separating the resultant styrene by distillation. This is very apparent if the boiling points of the components concerned are examined (see Table 1). In the event superfractionation to recover ethylbenzene from the  $C_8$  aromatics stream and then dehydrogenate to styrene would be more economic.

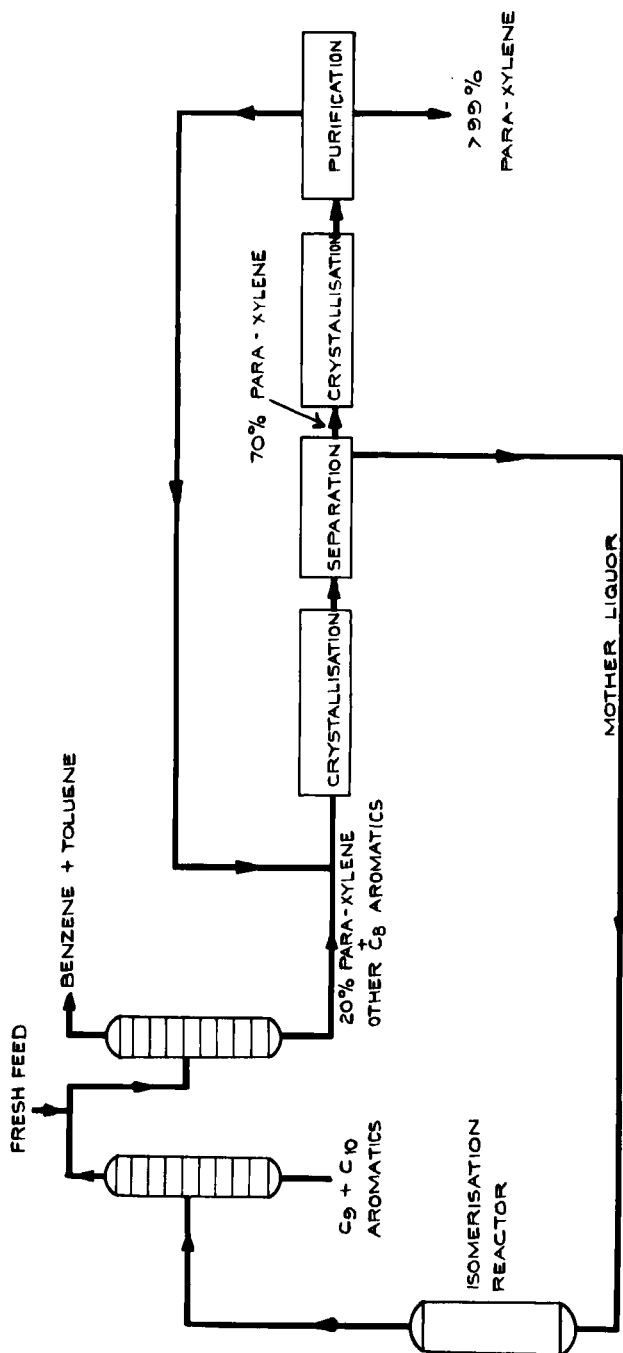


FIGURE 1

Schematic Outline of a Typical Para-Xylene Process

TABLE I

Boiling points of C <sub>8</sub> aromatics	
Component	Boiling Point °C
Ethylbenzene	136.19
Para-Xylene	138.35
Meta-Xylene	139.10
Ortho-Xylene	144.41
Styrene	145.14

In our circumstances selective extraction of styrene with aqueous silver fluoborate would appear to overcome the separation difficulty and afford an attractive process for styrene manufacture. After separation of styrene the mixed C<sub>8</sub> aromatics would be used as feed to the para-xylene process.

### III. Basic Outline of Process

The silver fluoborate process for styrene was considered to consist essentially of three stages (see Figure 2). Ethylbenzene and xylenes are fed into the reaction section where the ethylbenzene is dehydrogenated to styrene. The product from the reactor is fed to the separation stage where styrene is extracted from xylene using aqueous silver fluoborate as solvent in a liquid-liquid extraction process. Xylenes were expected to be present in the extract phase and would have to be removed in a purification stage to recover styrene of the required purity, >99.6%.

Work on the reactor stage was proceeding at the same time as that on the separation and purification stages. An iron oxide-steam catalyst system was used.

### IV. Separation Stage

The first step in the recovery of styrene from xylenes involved use of the liquid-liquid extraction technique using aqueous silver fluoborate (aq. AgBF<sub>4</sub>) as the extractant. A number of parameters were considered in order to provide the basic data required for design of such a unit.

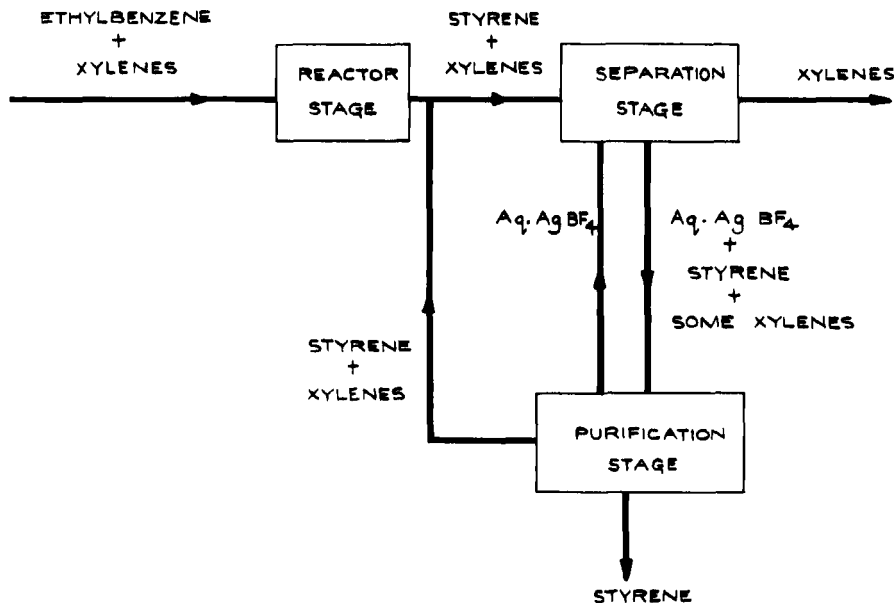


FIGURE 2

## Basic Outline of the Silver Fluoborate Process for Styrene

## A. COMPLEX FORMATION

Data available in the literature show that silver salts complex more strongly with styrene than with ethylbenzene or the xylenes (3)(4). Equilibrium constants,  $K$ , for the reaction  $\text{Ag}^+ + \text{Aromatic} \rightleftharpoons (\text{Ag Aromatic complex})^+$  are given in Table II. Preliminary experiments with  $\text{aq. AgBF}_4$  confirmed that styrene could be separated from admixture with xylene and ethylbenzene.

## B. EFFECT OF SILVER SALT CONCENTRATION

The effect of silver salt concentration was determined experimentally. The results in Figure 3 show that the partition equilibrium is appreciably affected by the concentration of the silver salt in the aqueous solution. Increasing the silver concentration favours dissolution of styrene in the aqueous phase. Furthermore, the amount of styrene extracted per unit of silver is greater the higher the concentration of silver in the solution.

RECOVERY OF STYRENE

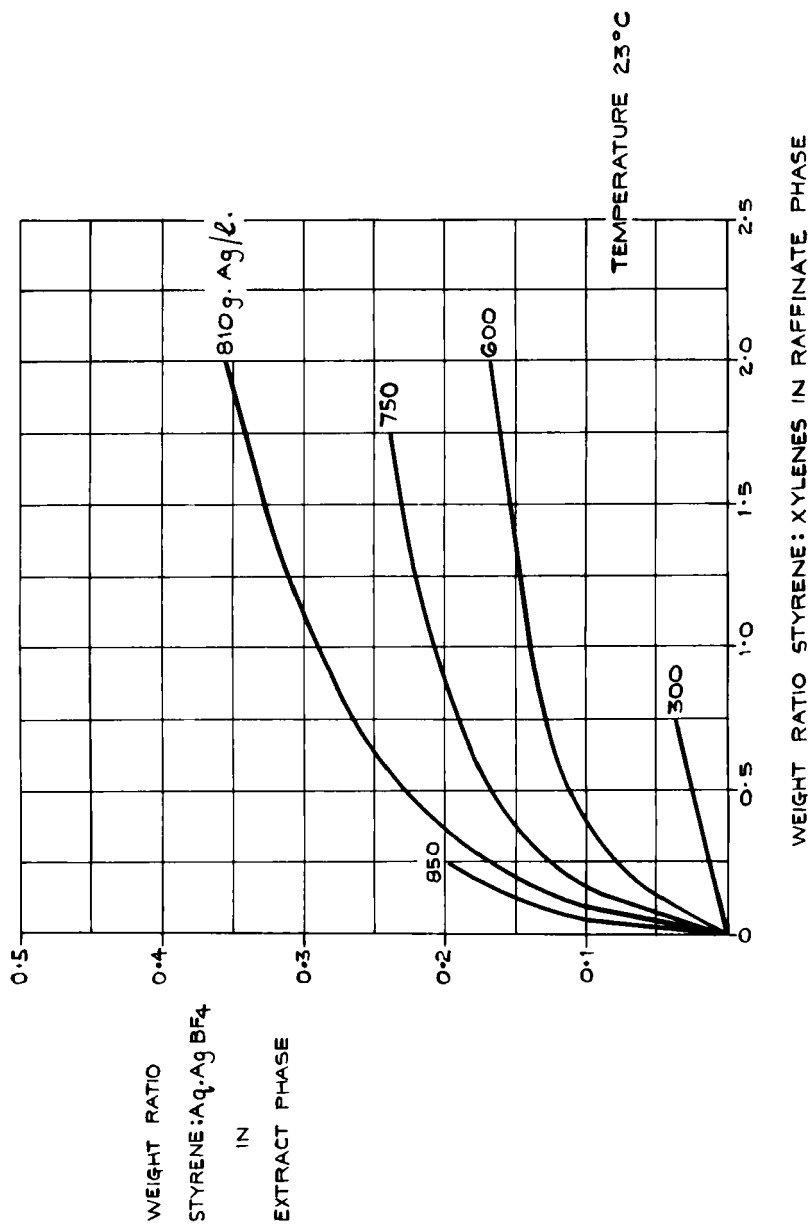


FIGURE 3  
Effect of Silver Salt Concentration



TABLE II

Equilibrium constants for complex formation.



Component	K
Para-xylene	2.63
Ethylbenzene	2.7
Ortho-Xylene	2.89
Meta-Xylene	3.03
Styrene	18.2

## C. EFFECT OF TEMPERATURE

The effect observed on changing the temperature at which the extraction was carried out is clearly shown in Figure 4. The lower the temperature the more styrene in the silver solution.

## D. EFFECT OF EXTRACTION TIME

Partition equilibrium of the styrene between the xylene and  $\text{aq. AgBF}_4$  phases was quickly attained. Shaking the hydrocarbon mixture with  $\text{aq. AgBF}_4$  for 30 seconds gave as good an extraction of styrene as that observed for a 10 minute mixing period. Phase separation was also quickly achieved.

## E. TERNARY DIAGRAMS FOR THE SYSTEM

STYRENE - XYLENES -  $\text{AQ. AgBF}_4$ 

The experiments to determine the effect of silver concentrations and of extraction temperature were extended to obtain ternary equilibrium diagrams for the system styrene-xylenes- $\text{aq. AgBF}_4$ . A typical diagram is shown in Figure 5. The system is a Type 2 system<sup>(5)</sup>, xylenes and styrene are partially miscible with  $\text{aq. AgBF}_4$ . The solubility of  $\text{aq. AgBF}_4$  in xylenes and in styrene is so low that it is difficult to represent this in Figure 5.

## F. LABORATORY LIQUID-LIQUID EXTRACTION UNIT

## 1. Design

The data collected were sufficient for design of a liquid-liquid extraction unit. The design was made using a standard graphical construction method<sup>(6)</sup> to determine the number of theoretical

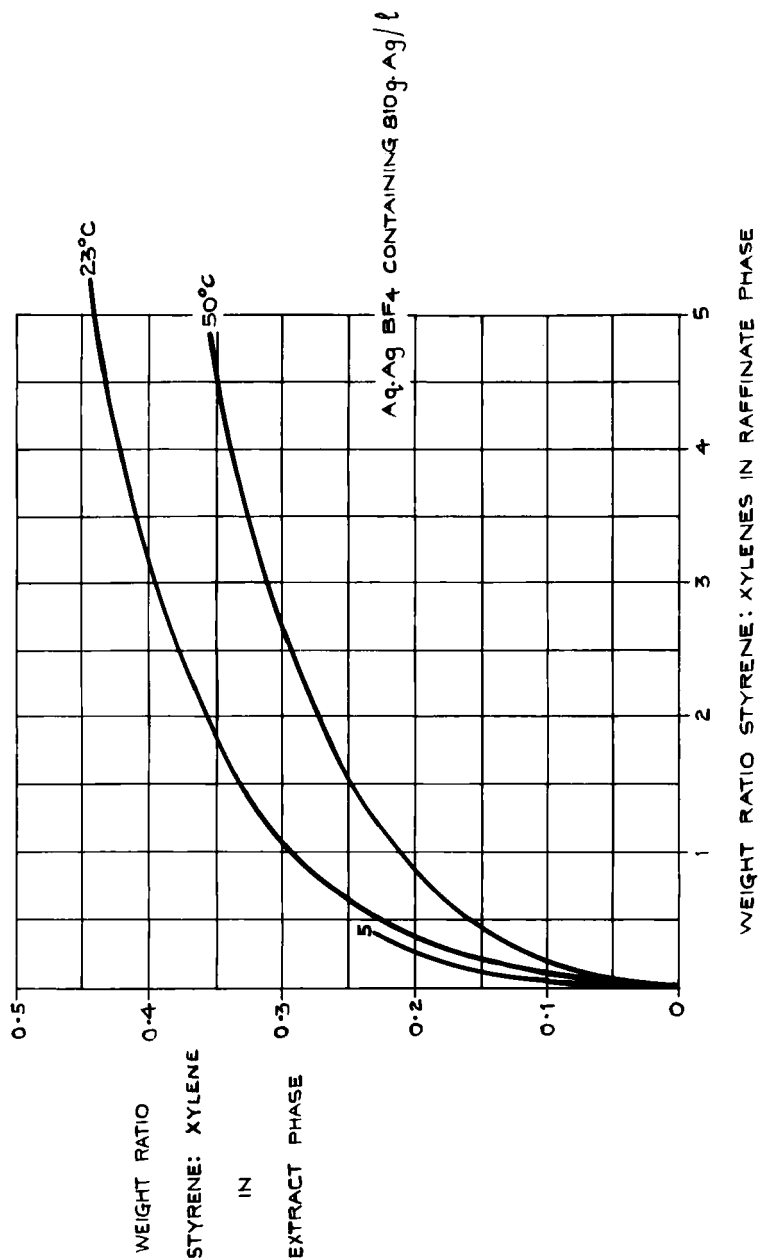


FIGURE 4  
Effect of Temperature

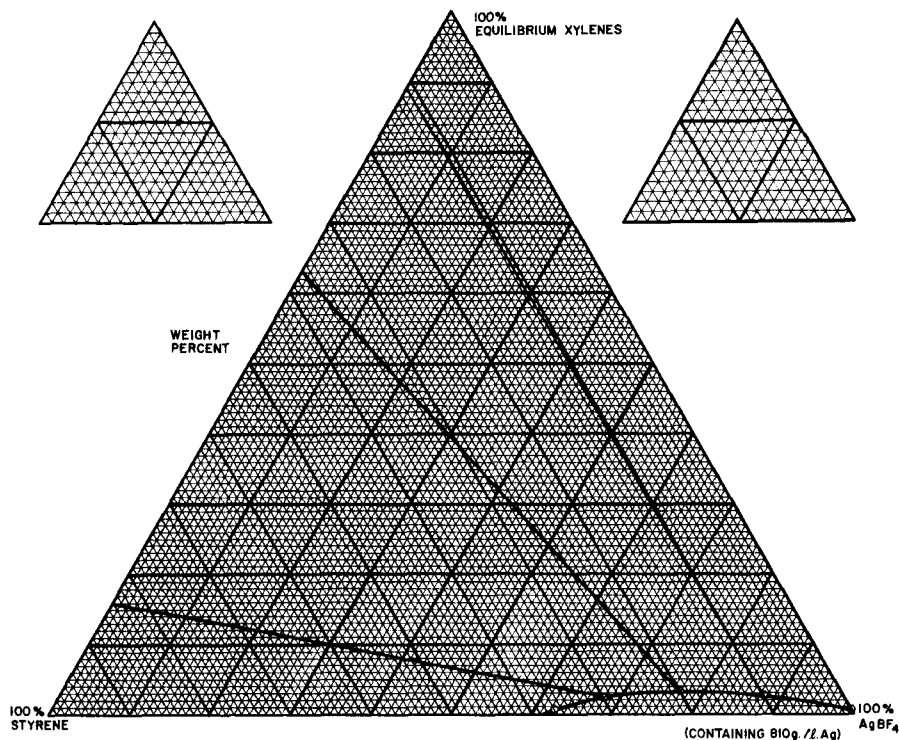


FIGURE 5

Ternary system: styrene - xylenes -  $\text{AgBF}_4$

stages required to effect the separation by countercurrent multi-stage extraction without reflux. In this way it was shown that 4 theoretical stages would be required to reduce the styrene content in the xylenes from 20% to 2%, using a silver solution containing 850 g.Ag/l. at 30 to 40°C. A solvent : feed ratio of 1.2:1 would be required. To achieve the same efficiency using the same number of theoretical stages and 580 g.Ag./l. solution the extraction temperature would have to be 0°C. This fact, together with the earlier finding that the amount of styrene extracted per unit of silver is greater the higher the concentration of silver

in the solution, led to the decision being taken that  $\text{aq. AgBF}_4$  containing 800 to 850 g.Ag/l would be used in the process.

## 2. Operation

A laboratory unit was assembled to check the design based on the equilibria data. It was anticipated that this unit would operate continuously to discover troubles that might arise from prolonged running, for example, deposition of silver in the system. An inverted 10 plate Oldershaw column, the type normally used in distillation, was used as the extraction column and worked admirably. Attempts to use such columns as liquid-liquid extraction units with other systems have not been so successful. Probably the large density difference between the silver solution and the hydrocarbon phase was responsible for the successful use of inverted Oldershaw columns in this work. A schematic outline of the continuous laboratory unit is shown in Figure 6.

$\text{Aq. AgBF}_4$ , containing 850 g.Ag/l., was fed into the top of the extraction column and 20% styrene in xylenes fed in at the bottom. Metering pumps were used so that the ratio of solvent : feed could be regulated. The interphase in the contractor was maintained at the top of the column with  $\text{aq. AgBF}_4$  as the continuous phase. The extract was flash distilled to recover the organics from the  $\text{aq. AgBF}_4$ . The organics distilled over as their azeotrope with water, this overheads product separated on cooling and the water rich phase was added to the regenerated  $\text{aq. AgBF}_4$  being recycled. All distillations were carried out at reduced pressure. The lower temperatures on the system thus curtail polymerisation of styrene and reduce the corrosive effect of the  $\text{aq. AgBF}_4$ . Initially with fresh  $\text{aq. AgBF}_4$  being fed to the contactor the raffinate contained <2% styrene. However, with continued operation using recycled  $\text{aq. AgBF}_4$  the styrene level in the raffinate began to increase. Further the amount of organics recovered in the flash distillation stage was much lower than anticipated, i.e. from that present in the aqueous phase according to equilibria data. Both observations led to the conclusion that the  $\text{aq. AgBF}_4$  extract phase

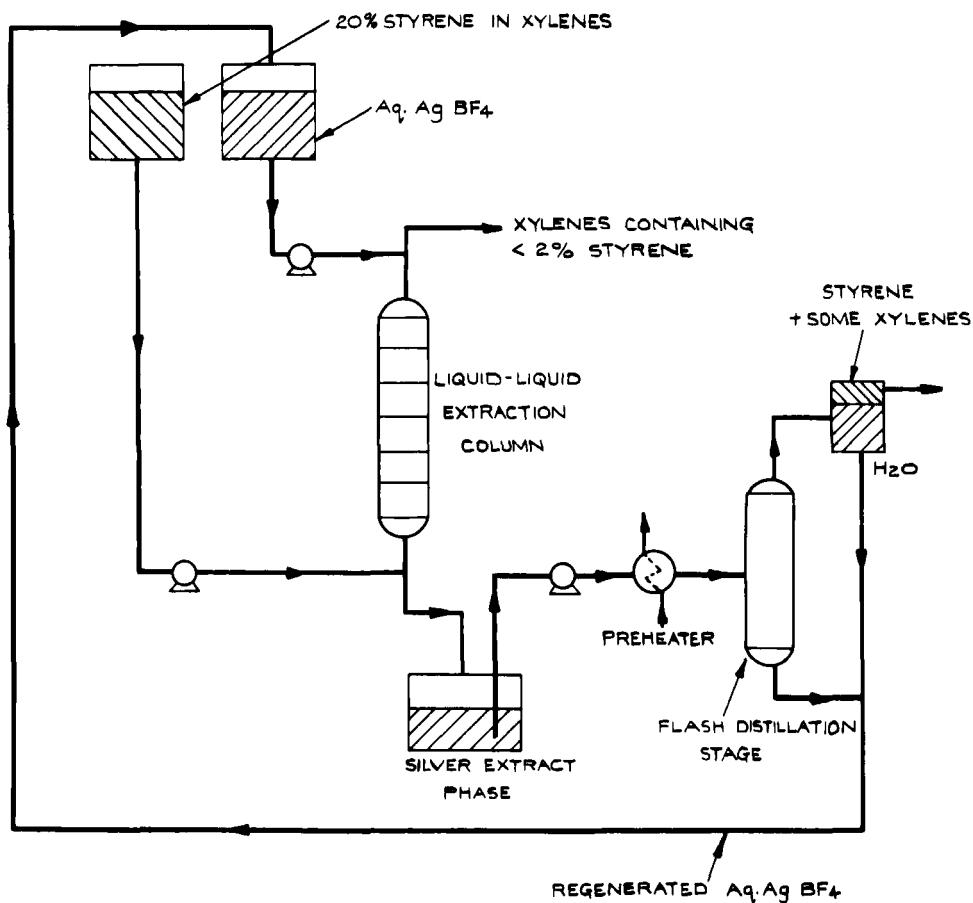


FIGURE 6

## Schematic Outline of Laboratory Unit 1

was not being completely stripped of organics in the flash distillation stage. However, if we accept a stage efficiency in the Oldershaw column of about 40%, the initial results had shown that the extraction column was working as had been predicted from equilibria data.

## V. Purification Stage

The ternary equilibrium diagram for a solvent containing 810 g.Ag/l at room temperature (see Figure 5) clearly shows that styrene of

only 80 to 90% purity is dissolved in  $\text{aq. AgBF}_4$  in equilibrium with mixed xylenes containing 20% styrene. Styrene of 99.6% purity is required. Therefore, as was originally envisaged, a purification step is necessary.

#### A. METHODS OF PURIFICATION

Several methods of purification were considered.

##### 1. Liquid-Liquid extraction with styrene reflux

As can be seen from the ternary diagram (Figure 5) the styrene concentration in the extract from mixed xylenes containing 20% styrene is only about 35% of that in equilibrium with pure styrene. Consequently a very high reflux of styrene would be required in the extraction stage and hence energy requirements would be very high.

##### 2. Two stage liquid-liquid extraction system

The organics recovered from the extract of the first liquid-liquid extraction unit could be fed to a second column of this type with a smaller flow of  $\text{aq. AgBF}_4$ . This could be a feasible method of purification as re-extraction of a feed containing 85% styrene would afford an aqueous phase containing 0.3 g. of organics/g. of Ag solution-the styrene content of the organics being 94%. The equivalent silver solution saturated with pure styrene contains 0.38 g of styrene/g. of Ag solution. The amount of pure styrene therefore required for reflux is reduced and could be reduced still further by operating the second extraction stage at an elevated temperature.

##### 3. Solvent exchange

The xylenes present in the extract phase could be replaced by a solvent from which styrene is easily separable, by refluxing the extract with, say, benzene. The silver solution would not differentiate between benzene and xylenes and the xylenes would be replaced.

##### 4. Extractive distillation

Batch distillations were carried out to investigate the earlier finding that organics were not removed completely from  $\text{aq. AgBF}_4$  by flash distillation under reduced pressure. Results showed that

the organic phase contained very much less than the expected 85% of styrene. Addition of water to the regenerated silver fluoborate solution and redistillation yielded a further quantity of styrene, this time of 95% purity. Obviously from the results of the batch distillations the volatility of xylenes to styrene is greatly enhanced in the presence of  $\text{aq. AgBF}_4$ . Thus purification could be accomplished by extractive distillation.

The above methods of purification were all considered and it was decided that extractive distillation would ensure that the purification was achieved simply and efficiently. This method was therefore studied more fully.

## B. PURIFICATION BY EXTRACTIVE DISTILLATION

### 1. Vapour-liquid equilibria data

Vapour-liquid equilibria data were required in order to design the extractive distillation column. However, the equilibrium stills available in Petrochemicals Division at that time were not satisfactory in handling vapours that condensed to two liquid phases. Only a limited number of measurements were therefore made in this way.

Vapour-liquid equilibria data were essential in order that the project be progressed. The method finally evolved was to calculate the data using the solubility data collected for the liquid-liquid extraction stage. This was done as follows.

In a system of  $\text{aq. AgBF}_4$  saturated with xylene and styrene the organic layer contains very little  $\text{AgBF}_4$  or water and the vapour above this layer will be almost identical with that above a similar organic mixture not in equilibrium with  $\text{aq. AgBF}_4$ . Assuming that xylenes and styrene form ideal solutions, i.e. Raoult's Law holds, then the partial pressures of xylenes and styrene can be calculated from their concentration in the organic layer and vapour pressure data. If the relationship between organic and aqueous layers is known from solubility data, i.e. tie-lines on a ternary diagram, then the relationship between vapour and saturated aqueous layer can be calculated. Hence the relative

volatility of xylene in saturated aq. $\text{AgBF}_4$  can be calculated. The relationship between vapour composition and saturated aqueous phase composition calculated in the above manner is shown in Figure 7. The results are for aq. $\text{AgBF}_4$  containing 810 g. $\text{Ag/l.}$  at a temperature of  $50^\circ\text{C}$ . The vapour-liquid equilibria relationship is for saturated solutions.

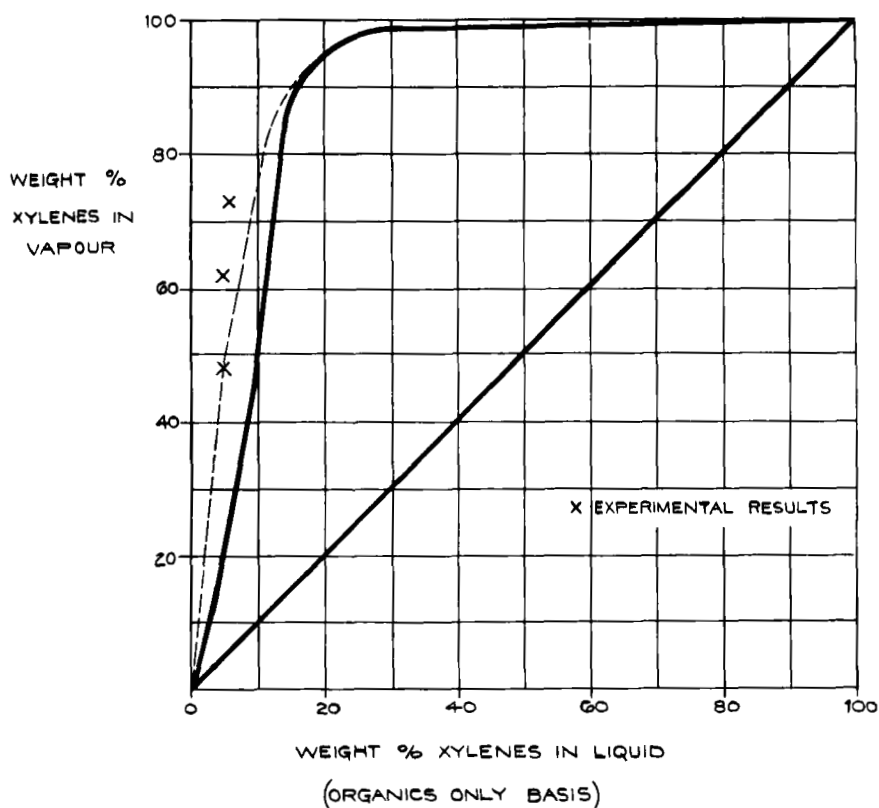


FIGURE 7

Estimated Vapour-Liquid Equilibria of  
Xylenes-Styrene in Presence of Aq. $\text{Ag BF}_4$   
(810g.  $\text{Ag/l}$ ) AT  $50^\circ\text{C}$



From theoretical reasoning, relating to complex formation between silver and styrene, it was considered that for unsaturated  $\text{aq.AgBF}_4$  the relative volatility of xylenes to styrene would be increased. This is illustrated diagrammatically in Figure 7 by the dotted line. The crosses are the few experimentally determined points mentioned earlier and these data fitted in well with the prediction made for  $\text{aq.AgBF}_4$  not saturated with organics. The separation of xylenes from styrene in the presence of  $\text{aq.AgBF}_4$  is so easy that even if the design is based on the line for saturated solutions, this will not greatly affect the number of plates required in an extractive distillation column.

2. Partial pressures above solutions of styrene in  $\text{aq.AgBF}_4$   
The observation that water had to be added to the extract phase for complete removal of styrene was then considered. It was felt that a quantitative explanation of this requirement would be forthcoming if the partial pressures of water and styrene above silver fluoborate solutions containing styrene, and xylene, were known. These partial pressures are best determined from vapour-liquid equilibria experiments. This was not possible because the right type of equilibrium still was not available (see Section V.B.1). The information was therefore derived from the data that existed and a few total pressure measurements. The method was as follows.

The total pressures of three  $\text{aq.AgBF}_4$  solutions saturated with styrene (i.e. two-liquid phase mixtures) were determined over the temperature range of interest. The organic layer was assumed to be pure styrene and hence the partial pressure of styrene above the two-liquid phase mixture is equal to the vapour pressure of pure styrene at the same temperature. The partial pressure of water above the mixture is therefore given by the difference between the total pressure above the mixture and the vapour pressure of pure styrene. The results are given in Figure 8, together with the vapour pressures of the  $\text{aq.AgBF}_4$  solutions which were also determined. The concentration of styrene in the

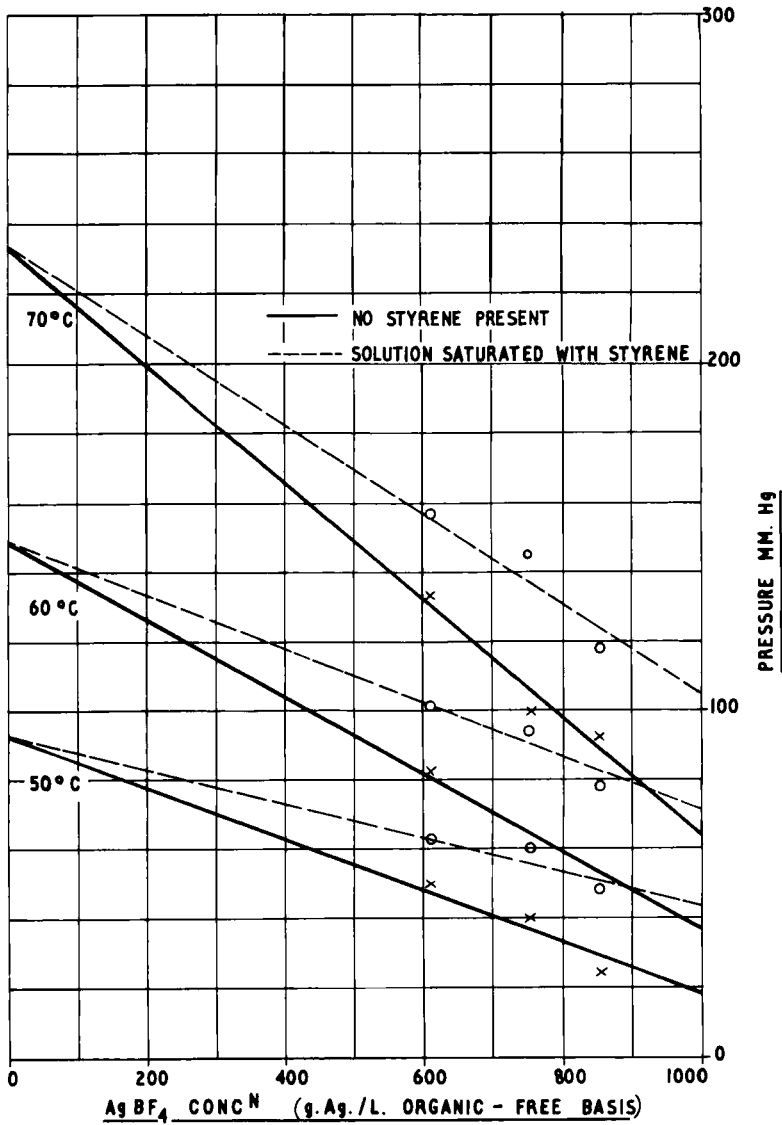


FIGURE 8

Partial Pressures of Water above  
Aqueous Silver Fluoborate/Styrene Mixture

saturated solution is not constant for a given temperature but is a function of the  $\text{AgBF}_4$  concentration. Using the solubility data collected for the separation stage Figure 9 was constructed. The results in Figure 9 show the variation (assumed to be linear) of the partial pressure of water with concentration of dissolved styrene for two  $\text{AgBF}_4$  concentrations at a number of temperatures. In addition to a knowledge of the partial pressures of styrene above  $\text{aq. AgBF}_4$  saturated with styrene, the partial pressure of styrene above solutions saturated with styrene-xylene mixtures can also be calculated (see Section V.B.1). From solubility results for  $50^\circ\text{C}$  the partial pressures of styrene above  $\text{aq. AgBF}_4$ -styrene solutions were calculated and are shown in Figure 10. Also shown in Figure 10 are the partial pressures of styrene above  $\text{aq. AgBF}_4$  saturated with styrene.

The partial pressures of water and styrene above an 810 g.Ag./l  $\text{aq. AgBF}_4$  solution containing styrene are therefore known approximately. Useful information of this nature was also derived from the results of batch distillations of styrene-xylenes- $\text{aq. AgBF}_4$  mixtures. The composition of the liquid in the boiler at the end of each fraction could be calculated from a knowledge of the original composition and the composition and amount of distillate. The data calculated from the batch distillations, along with those previously calculated for the 810 g.Ag./l solutions were used to construct Figure 11. Also given in Figure 11 are the vapour compositions above saturated styrene- $\text{aq. AgBF}_4$  mixtures which were calculated from Figure 8 and the vapour pressure of pure styrene. An approximate relationship had therefore been deduced between the partial pressures of styrene and water and the concentration of styrene and silver fluoborate in solution at  $50^\circ\text{C}$ . Similar relationships will exist at other temperatures.

The derived results presented in Figure 11 clearly show that for complete styrene removal it is necessary to replace the water lost as an azeotrope. If the silver concentration reaches about 1 200 g.Ag./l., the distillation of styrene ceases.

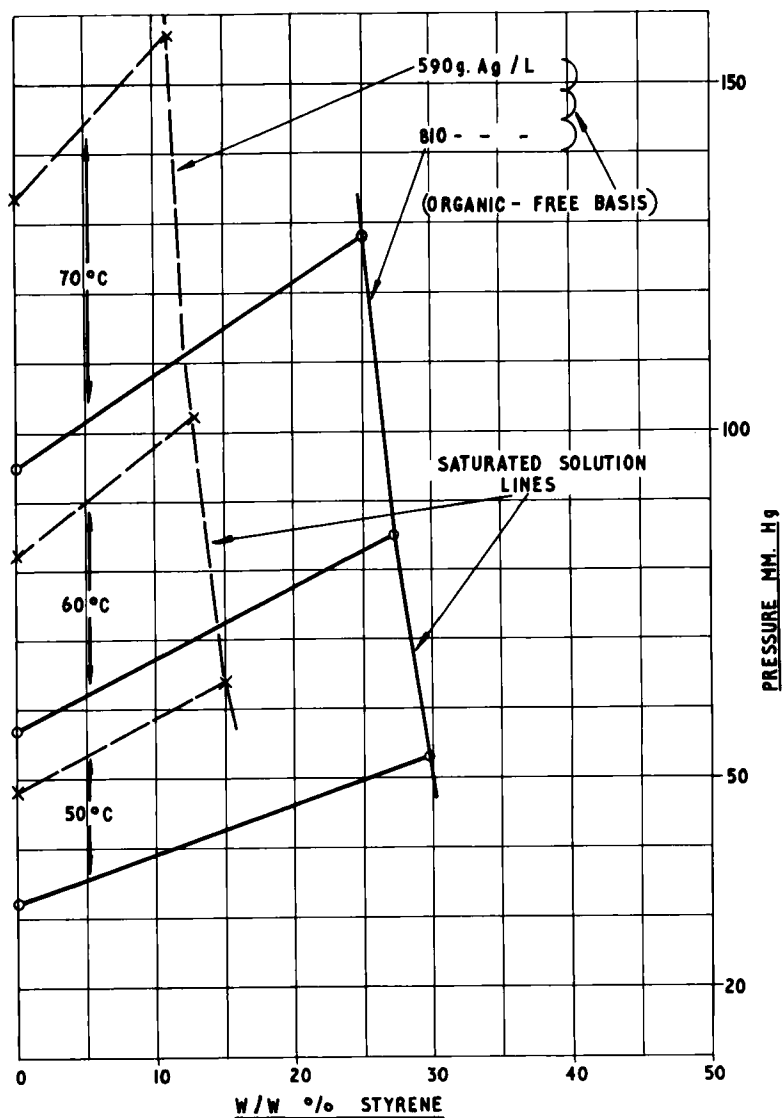


FIGURE 9

Partial Pressures of Water above  
Aqueous Silver Fluoborate/Styrene Mixtures

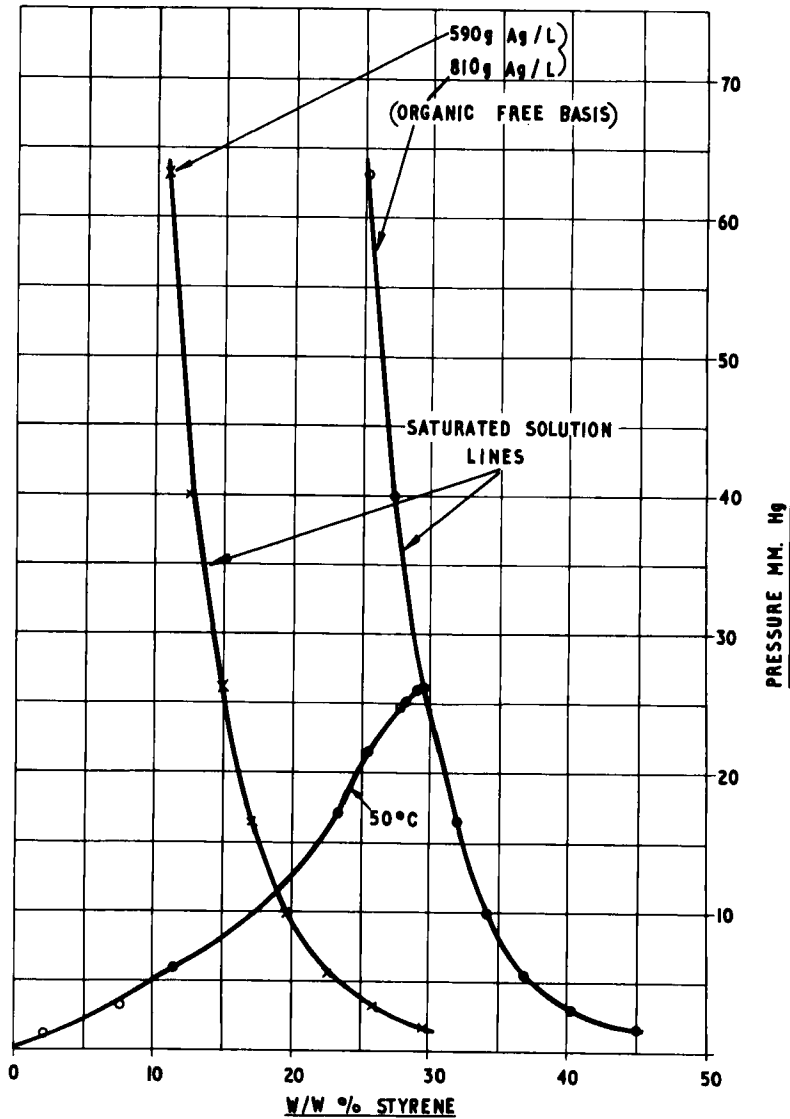


FIGURE 10

Partial Pressures of Styrene above  
Aqueous Silver Fluoborate/Styrene Mixtures

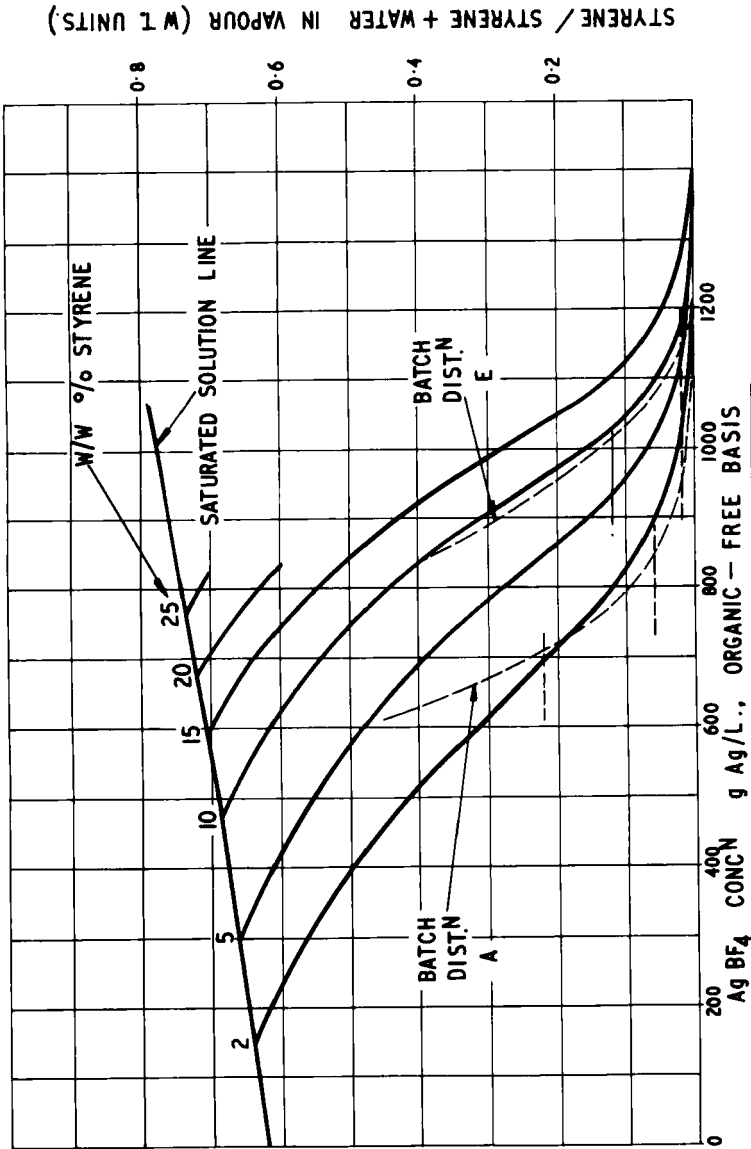


FIGURE 11  
Vapour Compositions above Aqueous Silver Fluoborate/Styrene Mixtures

Data were now available to design the extractive distillation stage. The calculated x-y diagram for xylenes-styrene in the presence of aq.  $\text{AgBF}_4$  and use of the McCabe-Thiele method <sup>(7)</sup> ascertained that 5 theoretical plates would be required in the extractive distillation column. Further it was decided to add the water necessary for complete styrene removal as steam and it was proposed that this would be most efficiently used in a counter-current stripping column.

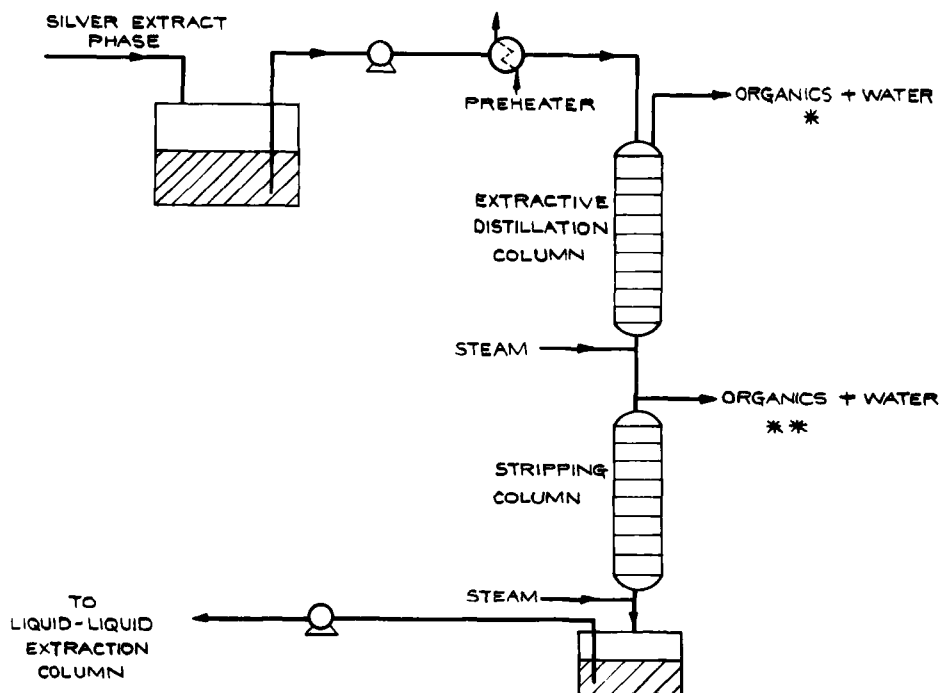
### C. LABORATORY UNIT 2

Using the data now available a continuous separation and purification unit was designed and constructed on a laboratory scale. The final version of the purification stage is shown schematically in Figure 12. The extractive distillation and stripping columns were built in Oldershaw plates. The stripping stage was required to give substantially complete removal of styrene from the aqueous extract. The extractive distillation column initially contained 10 plates, this was later increased to 20 plates because of the failure to produce, consistently, styrene of high purity.

In the first series of experiments steam was fed to the bottom of the stripping column at a temperature intended to be high enough to supply the heat requirements of the system and in an amount sufficient to replace the water lost in the organic-water azeotrope distillates. However, there was a large loss of organic material which was attributed to the formation of polymer in the steam stripping stage due to the rather high (95 to 100°C) operating temperatures.

To overcome this the unit was modified to the design shown in Figure 12 and steam introduced separately to the foot of the extractive distillation and stripping columns. The column temperatures could now be controlled more rigidly (at 90°C or below) and polymer formation was drastically reduced. High purity styrene was, of course, recovered as a side-stream. The organic distillate from the top of the extractive distillation column being returned

# RECOVERY OF STYRENE



\* ORGANICS CONTAINING 50 TO 70% STYRENE RETURNED TO LIQUID-LIQUID EXTRACTION COLUMN

\*\* ORGANICS CONTAINING ca. 99% STYRENE. PRODUCT STREAM.

FIGURE 12

## Schematic Outline of Laboratory Unit 2

to the liquid-liquid extraction column. Typical results from this unit are shown in Table III. Important points to note are as follows.

- a) The styrene purity reached nearly 99%. The impurities then consisted of polymer and some benzaldehyde, these were easily removed by side-arm distillation and styrene of 99.8% purity obtained. A final distillation will therefore be necessary



TABLE III  
Typical results from Laboratory Unit 2.

Run No	Liquid-Liquid Extraction Stage		Distillation of silver extract phase					Conc.* of AgBF <sub>4</sub> in bottoms g.Ag/l		
	Vol.Ratio Organics: Aq.AgBF <sub>4</sub>	%w/w Styrene in	Feed	Vol.of water added per vol. of Ag extract	Press mms	Distillate % w/w Styrene in			Recovery of Styrene 98.75% purity (as % w/w of organics in extract)	
						Raffinate	Side-stream			
										Tops
# 4	1:1	20.5	2.1	0.75:1	150	55	99.0	41	81	664
# 6	1.2:1	20.5	1.1	0.85:1	150	58	97.3	32	66	660
# 10	0.95:1	45.0	2.6	0.7:1	210	75	98.8	43	98	550
# 11	0.6:1	52.0	3.0	0.5:1	210	72	99.0	42	95	540
# 12	1:1	13.6	1.0	0.6:1	210	69	98.8	39	92	632

\* The aq.AgBF<sub>4</sub> used initially contained 800 to 850 g.Ag/l.  
† Steam fed into distillation stage at bottom of stripping column.  
‡ Steam fed into column at two points.

as in conventional styrene plants, where this is done immediately prior to use. Topping will also be necessary if the styrene is required dry.

- b) In the laboratory it was found impossible to avoid diluting the silver solution, and an evaporator to concentrate the solution may be necessary in a plant.

#### VI. Miscellaneous Work

While the mainstream work was being progressed, several other important aspects were being considered.

#### A. LOSSES IN THE SYSTEM

##### 1. Silver deposition

The decrease in silver concentration of silver fluoborate solutions was measured in the course of the operation of the continuous separation and regeneration system (see Figure 6) and results are given in Table IV. The results show that silver deposition could be a serious problem in this process. However, a further experiment in which hydrogen peroxide was added to the  $\text{aq. AgBF}_4$  at a rate of 0.1% volume/volume/hour gave no measurable change in silver concentration<sup>(8)</sup>.

Deposition of silver was subsequently avoided in operation of the continuous laboratory units by the prior addition of 1% by weight hydrogen peroxide to the silver solution. Further additions were made if any darkening of the silver solution was observed.

TABLE IV

Observed changes in silver concentration  
during operation of Laboratory Unit 1.

Boiler temp. Duration of Silver concentration (g./l.)			
°C	run hrs.	Initially	Finally
47	23	836	742
49	24	798	730
53	22	779	682

## 2. Polymerisation of styrene

1 to 2% of the styrene was lost by polymer formation in the stripping column present in the purification stage of the laboratory unit. This could possibly be prevented by the addition of an inhibitor to the aqueous extract. The effect of inhibitor and hydrogen peroxide in the same solution would have to be evaluated.

## 3. Formation of benzaldehyde

Hydrogen peroxide, added to stabilise the silver solution, reacted with the styrene and formed benzaldehyde. This was present in small amounts, 0.2 - 0.4% w/w, in the styrene from the side-stream take-off in the purification column.

## B. RAFFINATE TREATMENT

It was necessary to find out if the raffinate stream (mainly xylenes) from the extraction column required treatment before it could be fed to the para-xylene process.

### 1. Hydro-refining

It was shown that 1 to 2% styrene caused excessive carbon lay-down in the reactor in the para-xylene process. Reduction of the styrene content in the raffinate to the parts per million level acceptable in the feed to the para-xylene process was not practicable by extraction with aq. $\text{AgBF}_4$ . This would require the use of an uneconomical amount of aq. $\text{AgBF}_4$  or an impractical number of stages in the extraction column. The simplest way to remove residual styrene was by hydrogenation. Several catalysts were found to be suitable, the best one being 68% nickel oxide on Kieselguhr.

### 2. Removal of silver

The raffinate also contains 100 to 500 p.p.m. silver, which might be harmful to the xylene isomerisation catalyst, and which would in any case be worth recovering. It was shown that the silver could be removed by flash distillation of the xylenes or by water washing.

### C. MATERIALS OF CONSTRUCTION

A major problem from the point of view of process design was the choice of materials of construction for use with the highly corrosive silver fluoborate solution.

#### 1. Corrosion tests on metals

Corrosion tests were carried out by heating metal specimens in aq.  $\text{AgBF}_4$  solutions containing xylenes and styrene. Although acceptable corrosion rates may vary from one project to another, a rate of 1mm/year is usually considered to be excessively high, and 0.1 mm/year is satisfactory. With these figures in mind the results of the tests showed that titanium had a high corrosion rate, 18/10/Mo/Ti would probably be acceptable at 50°C, platinum and tantalum are resistant to attack.

#### 2. Electro-chemical tests

Because of the high cost of platinum and tantalum attempts were made to reduce corrosion rates of austenitic steels and other alloys by the application of anodic passivation. It was deduced from potential/current curves that, at room temperature, anodic protection could be applied to 18/10/Mo/Ti, and at 50°C there was still a tendency to passivity.

#### 3. Tests on non-metals

Non-metallic materials were tested by placing specimens in the liquid and vapour phases of a refluxing solution of a silver extract. The results indicated that, apart from Fluon, the satisfactory linings are of the phenol-formaldehyde resin type, for example, Lithcote, Durestos, Ferrobestos, and Tufnol. These resins appeared to be satisfactory even at a temperature of 90°C.

#### 4. Tests with boilers

The results from the tests on metal specimens at 50°C had shown that 18/10/Mo/Ti was on the borderline of an acceptable corrosion rate of 0.1 mm/year. At this stage of the work it was envisaged that the maximum temperature in the process would be 50 to 60°C. A small boiler of 18/10/Mo/Ti and also one of a similar steel

18/8/Ti were ordered in order to evaluate corrosion effects. However, before the boilers arrived it had become clear that temperatures of 70 to 90°C would be reached in the system. A mild steel boiler was then fabricated and coated with Lithcote. A silver extract phase, containing 850g.Ag/l, was placed in each of the three boilers and refluxed for 150 hours. The results showed that the boiler in 18/10/Mo/Ti had a borderline corrosion rate at 50°C; that in 18/8/Ti appeared slightly more resistant to attack; the Lithcote lined boiler was satisfactory at 80 to 85°C.

#### VII. Summary

The laboratory reaction, separation and purification arrangement did not provide an exact model for plant design. However, it was felt that the arrangement was sufficiently close to demonstrate that styrene of the desired purity could be obtained simply, and as a costing showed a 15% return on the total capital employed, with reasonable economy.

Therefore the process to recover styrene with silver fluoborate solutions was, for a specialised requirement, economic. Why is there no process operating on a production scale? As so often happens in industrial research projects the commercial situation changed as the 6 months programme of work reached a close. A week or two from the end of the target date I.C.I. was offered, on reasonable terms, a C<sub>8</sub> aromatic feed containing less than 5% ethylbenzene. The incentive to build a process therefore disappeared.

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