REFINING OF BENZENE SULFONYL CHLORIDE FROM BENZENE-CHLOROSULFONIC ACID SULFONATION MASS

by

Julius H. Bochinski

and

Eugene B. Gach

A thesis submitted in partial fulfillment
of the requirements for the degree of
Bachelor of Chemical Engineering
in the
College of Engineering
of the
University of Detroit

June 1950

PREFACE AND ACKNOWLEDGEMENT

In the production of benzene sulfonyl chloride by the direct chlorosulfonation of benzene with chlorosulfonic acid and the subsequent treatment of the sulfonation mass, operating precautions taken to prevent hydrolysis losses made the process inefficient and uneconomical.

The purpose of this thesis was to devise a method of production by investigating the important factors involved and by applying the results of this investigation.

The authors wish to acknowledge Dr. Charles G. Duncombe, Director of the Department of Chemical Engineering, for his helpful suggestions and criticism and Messrs. Henry Gudebski, Charles Rebert, and Hugh Forresburg for their assistance in obtaining the laboratory equipment used. Acknowledgement is also given to Messrs. Fred Smith and Lawrence Healy of the Pilot Plant of the Wyandotte Chemicals Corporation for furnishing the benzene-chlorosulfonic acid sulfonation mass.

TABLE OF CONTENTS

ABSTRACT

This thesis represents the investigations and application of various chemical and engineering principles that may prove useful in designing an efficient and economical method for producing benzene sulfonyl chloride from benzene-chlorosulfonic acid sulfonation mass.

Phase separation of the sulfonation mass with water followed by countercurrent extraction of the acids from the sulfonation mass proved to be a more efficient and economical process than a batch drowning process.

Centrifuging and low temperature vacuum distillation of the benzene sulfonyl chloride emulsion appeared to be efficient method of clarification.

In brief, the conclusion summary was outlined as follows:

In the refinement of benzene chlorosulfonic acid sulfonation mass, the continuous agitated-phase-separation and counter-current extraction process with

clarification by centrifuging and vacuum distillation appeared much more efficient than the batch-drowning process for

- I Hydrolysis losses
  - a) were not greatly increased by agitation
  - b) were reduced for use of smaller volumes of drowning water,
  - c) were repressed in agitated phase separation
  - d) were less when the wash water was more efficiently used
  - e) were less when proper temperature control was obtained
  - f) were reduced as the period of contact with water was shortened
- II Entrainment losses were reduced by
  - a) use of less water overflow
  - b) the action of the column packing
- III Clarification was made possible
  - a) by removal of water by centrifuging
  - b) by removal of water by vacuum distillation
- IV Man-hours were more efficiently used by
  - a) reducing the process time
  - b) reducing requirements for rigid control

STATEMENT OF PROBLEM

To devise an efficient and economical method of producing a clear benzene sulfonyl chloride product with minimum amounts of water, acids, and other objectionable impurities from a benzene-chlorosulfonic acid sulfonation mass.

SCOPE OF PROBLEM

The treatment of this problem involved the development of a method for the refining of benzene-chlorosulfonic acid sulfonation mass into a clear benzene sulfonyl chloride product by removing the contained acids and introduced water. The refining method devised had low hydrolysis losses, low entrainment losses, an improved overall efficiency and industrial application. These factors were investigated on a laboratory scale with emphasis on increasing yield and reducing operation cycle time. No attempt was made to remove the diphenyl sulfone by-product.

CHAPTER I

INTRODUCTION

Although the compound was known for many years, benzene sulfonyl chloride did not become listed as a commercially produced chemical until recently. The full commercial possibilities have not been fully explored as yet, but it was expected that this chemical would find wide use in synthesis of organic compounds and preparation of dyestuffs, pharmaceuticals and plasticizers.

Benzene sulfonyl chloride had been prepared by the following methods: by the action of phosphorus pentachloride or phosphorus oxychloride on sodium benzenesulfonate; by the action of phosphorus pentachloride on diphenyl sulfone; by the action of chlorine on benzenesulfonic acid; by the action of chloride on diphenyl sulfoxide; by the action of sulfonyl chloride on benzene; and by the action of benzene on chlorosulfonic acid.

In the reaction of benzene on chlorosulfonic acid the following reactions may take place simultaneously;

$$C_6H_6 + HSO_3Cl \longrightarrow C_6H_5SO_3H + HCl$$

$$C_6H_5SO_3H + HSO_3Cl \longrightarrow C_6H_5SO_2Cl + H_2SO_4$$

$$C_6H_6 + HSO_3Cl \longrightarrow C_6H_5SO_2Cl + H_2O$$

$$HSO_3Cl + H_2O \longrightarrow H_2SO_4 + HCl$$

$$C_6H_5SO_2Cl + C_6H_6 \longrightarrow C_6H_5SO_2H_5C_6 + HCl$$

The benzene-chlorosulfonic acid reaction produced a reaction mass which contains benzene sulfonyl chloride, sulfuric acid, hydrochloric acid, and diphenyl sulfone with traces of benzene sulfonic acid and other side reaction products.

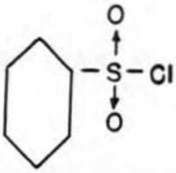
The benzene-chlorosulfonic acid reaction was used for commercial production by the Wyandotte Chemicals Corporation. The investigators, former employees of the company, decided to attempt to devise an economical and efficient method of producing a clear benzene sulfonyl chloride with minimum amounts of water, acid, and other objectionable impurities.

Tentative specifications of the commercial grades of benzene sulfonyl chloride and illustrative reaction equations were presented by the Wyandotte Chemicals as listed on the following sheets.

TECHNICAL
DATA
ON

Wyandotte

Benzenesulfonyl Chloride



TENTATIVE SPECIFICATIONS

Properties	Technical Grade	Refined Grade
Color	Amber liquid	Amber liquid
Purity	90% min.	99.0% min.
Melting Range	8.0° C—14.5° C	14.2° C—15.8° C
Distillation Range (40 mm)	135-157° C (95% over)	148-152° C (95% over)
Free Acid (as sulfuric acid)	0.25% max.	0.20% max.
Moisture	0.50% max.	0.2% max.
Phenyl Sulfone	10.0% max.	0.2% max.
Specific Gravity at 60° F	1.360-1.385	1.375-1.390
Weight per gallon at 60° F	approx. 11.4 lbs.	approx. 11.5 lbs.

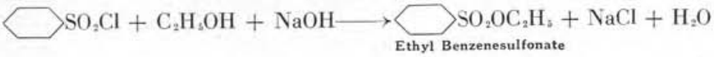
CHEMICAL PROPERTIES

Wyandotte benzenesulfonyl chloride reacts as a typical acid chloride and under certain conditions it may act as a chlorinating or oxidizing agent. Because of the low solubility of benzenesulfonyl chloride it is very slowly hydrolyzed by cold water, but strong alkalis or concentrated acids may be used in effecting rapid hydrolysis. Benzenesulfonyl chloride is useful for the preparation of esters, benzenesulfonamide, N-alkylated benzenesulfonamides, sulfinates, hydrazides and a variety of other synthetic products. It is a useful reagent for blocking active hydroxyl and amino groups.

Benzenesulfonyl Chloride

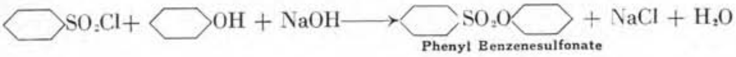
FORM 1149

1. Reaction with alcohols for the preparation of alkyl esters.



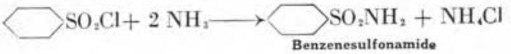
Ethyl Benzenesulfonate

2. Reaction with phenols for the preparation of aromatic esters.



Phenyl Benzenesulfonate

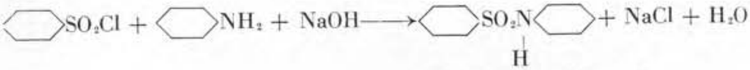
3. Reaction with ammonia to form benzenesulfonamide.



Benzenesulfonamide

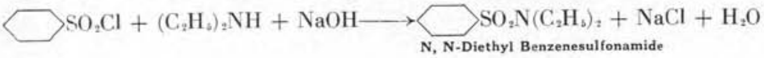
4. Reaction with primary amines to form N-monosubstituted benzenesulfonamides.

N-Ethyl Benzenesulfonamide

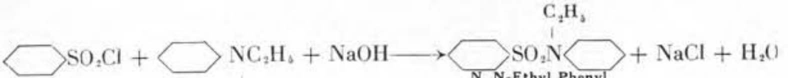


N-Phenyl Benzenesulfonamide

5. Reaction with secondary amines to form N, N-disubstituted benzenesulfonamides

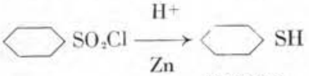


N, N-Diethyl Benzenesulfonamide



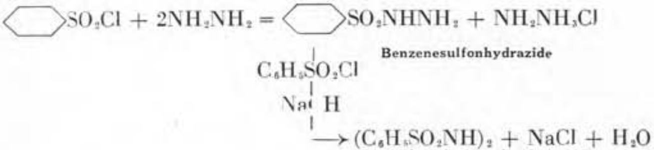
N, N-Ethyl Phenyl Benzenesulfonamide

6. Reaction with reducing agents (e.g. Zn and H_2SO_4) to form thiophenol



Thiophenol

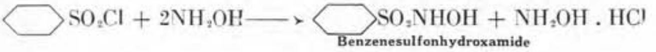
7. Reaction with hydrazine to form hydrazides.



Benzenesulfonhydrazide

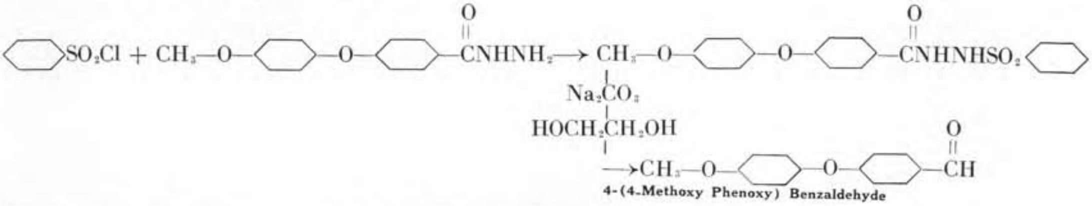
Bis (Phenylsulfonyl) Hydrazide

8. Reaction with hydroxylamine to form benzenesulfonhydroxamide.



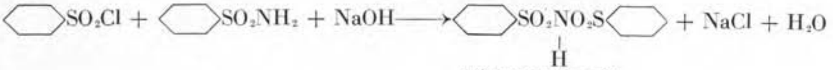
Benzenesulfonhydroxamide

9. **Reaction with N-aryl hydrazides to form aldehydes.**



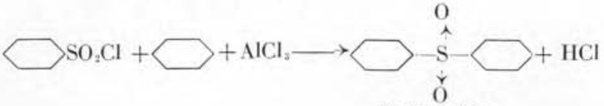
4-(4-Methoxy Phenoxy) Benzaldehyde

10. **Reaction with benzenesulfonamide to form dibenzenesulfonamide.**

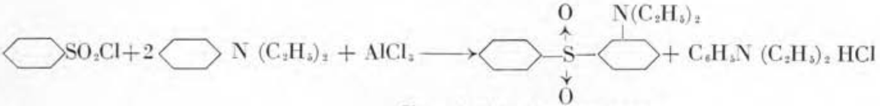


Dibenzenesulfonamide

11. **Reaction in Friedel-Krafts syntheses.**

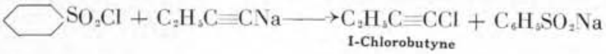


Phenyl Sulfone



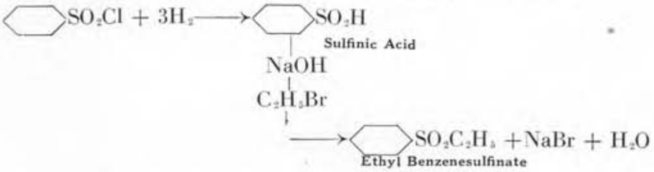
Phenyl Diethylaminophenyl Sulfone

12. **Reaction as a chlorinating agent for substitution of chlorine in unsaturated compounds.**



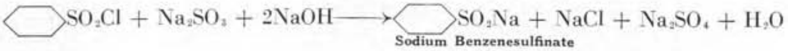
I-Chlorobutyne

13. **Reactions for the preparation of sulfinic acid and sulfinates.**



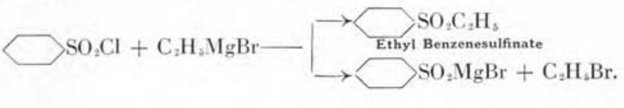
Sulfinic Acid

Ethyl Benzenesulfinate



Sodium Benzenesulfinate

14. **Reaction with Grignard reagents.**



Ethyl Benzenesulfinate

The reactions herein suggested are for illustration only and no representation of freedom from patent liability is warranted.

CHAPTER II

RELATED LITERATURE AND PRIOR EXPERIENCE

RELATED LITERATURE

The amount of published pertinent literature concerning benzene sulfonyl chloride was very meager, but a search of the library revealed some information.

According to Hans T. Clarke

Hans Thacher Clarke, Organic Synthesis, John Wiley and Sons, New York City, Volume X, pp 6-8, 1930.

benzene sulfonyl chloride was prepared in the following manner:

Benzenesulfochloride

$$C_6H_6 + 2ClSO_3H \longrightarrow C_6H_5SO_2Cl + H_2SO_4 + HCl$$

Submitted by H. T. Clarke, G. S. Babcock, and T. F. Murray. Checked by Frank C. Whitmore and A. M. Griswold.

1. Procedure

In a 5-l. flask, fitted with stirrer, dropping funnel, exit tube, and thermometer, is placed 3,500 g. (30 moles) of chlorosulfonic acid (Note 1), and to it is slowly added, with continuous stirring, 780 g. (10 moles) of benzene (Note 2), keeping the temperature between 20°C and 25°C by means of cold water. The hydrogen chloride which is evolved is led to a hood or absorbed in water. The addition requires two to three hours; when this is complete, the mixture is stirred for an hour, and poured onto 6-7 kg. of crushed ice (Note 3). One liter of carbon tetrachloride is then added, the oil is separated as soon as possible (Note 4), and the watery layer is shaken with 500 cc. of carbon tetrachloride. The combined oil is washed with dilute sodium carbonate, and the bulk of the carbon tetrachloride is distilled under atmospheric pressure (Note 5); the pressure is then reduced

(Note 6) and the benzenesulfochloride collected at 113-115°/10 mm. (118-120°/15 mm.). The yield is 1320-1360 g. (75-77 per cent of the theoretical amount) of a colorless liquid which on cooling sets to a crystalline solid melting at 13-14°.

A small amount (50-100 g.) of a higher boiling material remains in the flask. This is mainly diphenyl sulfone, which may be isolated by distillation under reduced pressure (b.p. 225°/10 mm.) and recrystallization from methyl alcohol. It forms colorless crystals which melt at 128°.

2. Notes

1. If less than 50 per cent excess of chlorosulfonic acid is taken, the yield of diphenyl sulfone increases at the expense of the sulfochloride.

2. A good commercial grade of benzene, boiling over a 1° range, is satisfactory. The benzene must be added to the acid (not vice versa); otherwise, a larger proportion of sulfone is formed.

3. The benzenesulfochloride separates at first as a crystalline solid which melts as the temperature rises. It was found impractical to filter off this solid, owing to its tendency to melt on the funnel.

4. The sulfochloride should be removed from the water as soon as possible; otherwise, the yield falls, owing to hydrolysis. In one run in which the mixture was allowed to stand overnight before separating, only 1220 g. (69 per cent) was obtained. If difficulty is experienced in the separation, owing to the presence of suspended solid matter, the oil may first be filtered with suction through a hardened paper or felt cloth. As a rule, it is merely necessary to filter the sludgy layer lying between the oil and the water.

5. The carbon tetrachloride vapor carries with it any moisture that may be present. If this were not removed at a relatively low temperature, hydrolysis of the chloride would take place, with the formation of sulfonic acid which would promote decomposition of the sulfochloride during its distillation.

6. The pressure should be reduced gradually, and the first runnings, mainly carbon tetrachloride, collected separately.

A German patent

Saccharinfabrik Akt-Ges., Vorm. Fahlberg, List and Co., Salbke-Westerhüsen A/E. Ger. pat. 224,386; Nov. 7, 1908. (Chemical Abstracts by American Chemical Society. Vol. 5, Jan.-April. p. 154, (1911).)

was found which involved the benzene-chlorosulfonic acid reaction. The abstraction was as follows:

> In the breaking up of a reaction mixture containing free chloro-sulfonic acid, the reaction mixture can without prejudice to the yield, be so broken up that gaseous HCl and high % H_2SO_4 of about 50° Be result. If a small amount of H_2O is led directly into the reaction mixture the reaction can be so controlled without material increase of the temperature, that from the excess chlorosulfonic acid employed all the HCl escapes in the gaseous form, while with a further addition of H_2O an oily layer, e.g., toluene sulfonyl chloride separates on the H_2SO_4 of 50° Be and is easily separated therefrom. Instead of a waste mixture of aqueous HCl and aqueous H_2SO_4, dry HCl gas and H_2SO_4 are obtained by this method of decomposition. Instead of adding H_2O for the breakup of the reaction mixture, aqueous HCl may be added.

Concerning the hydrolysis of benzene sulfonyl chloride, in a study conducted by Wilson, Fuller and Schur

R. E. Wilson, E. W. Fuller, and M. C. Shur. "Acceleration of the Hydrolysis of Mustard Gas by Alkaline Colloidal solutions". Journal of the American Chemical Society. Vol. 44, pp 2762-83 (1922.)

it was found that the mechanism of the hydrolysis of benzenesulfonyl chloride was similar in many respects to that of mustard gas. They stated that the effect of stirring, the formation of a cloudy layer near the interface, all indicated that these colloidal droplets in which the chloride was soluble accelerated the rate of solution in a manner exactly similar to that demonstrated for the case of mustard gas. The hydrolysis of benzene sulfonyl chloride was apparently catalyzed in the aqueous phase by the presence of hydroxyl ions and showed no evidence of reversal in acid solutions. Acid solutions of various colloids showed a similar accelerating tendency in cases where benzene sulfonyl chloride was soluble in the colloidal phase.

The following information was released from the files of the Pilot Plant of the Wyandotte Chemical Company.

According to David Bateman's report, the following excerpts were noted:

David F. Bateman, Research Division Report 608
Wyandotte Chemicals Corporation, March 17, 1948.

Item 2b. Stability

Stable in no excess water or acid. Hydrolysis slowly in acid content over 0.30% with over 1.0% water. Accelerated by increase of temperature.

Item 5. Temperature During Drowning

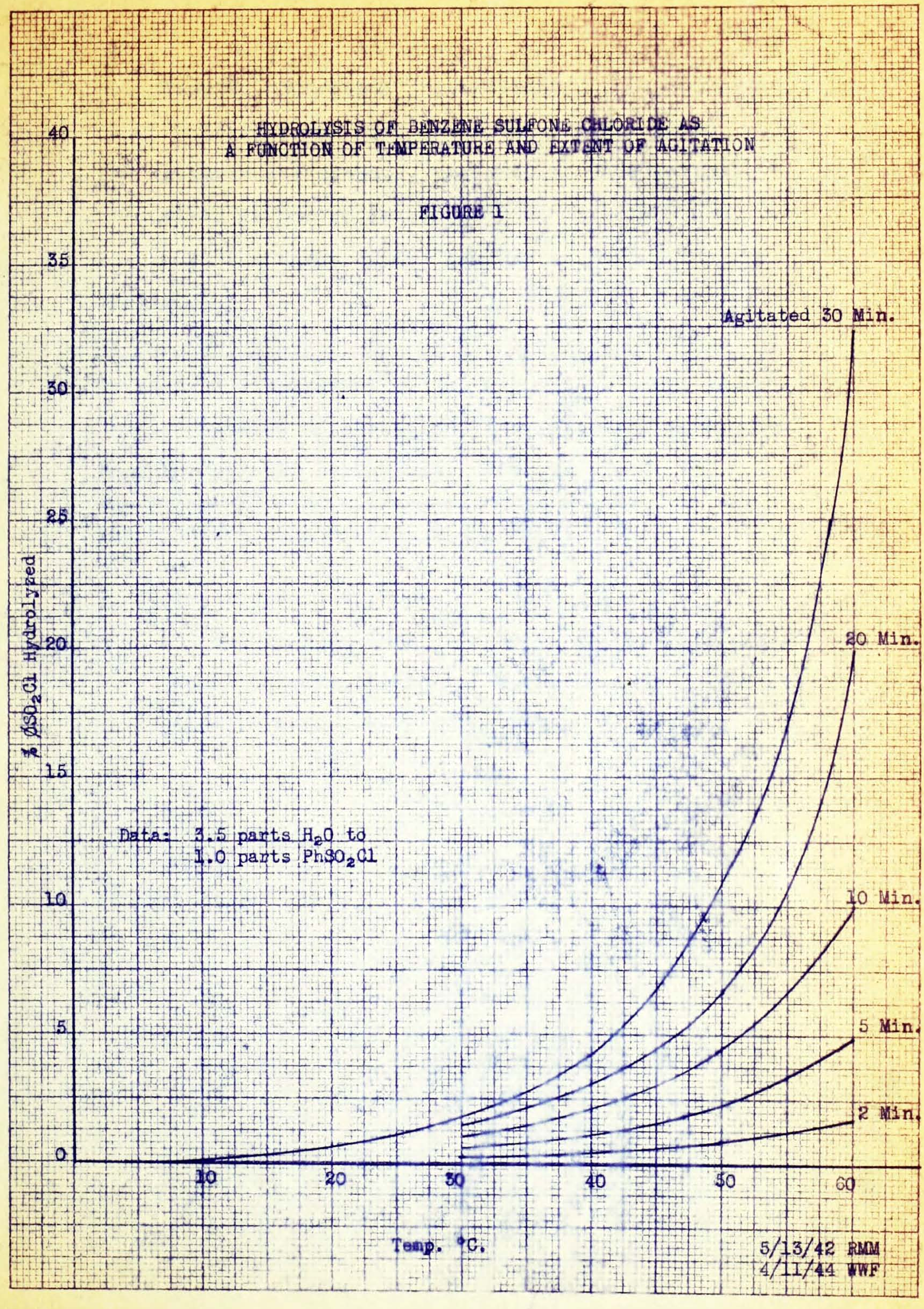
Temperatures above 40°C during drowning are to be avoided since higher temperature results in rapid hydrolysis of benzene sulfonyl chloride in presence of water with a significant drop in yield.

Temperatures below 20°C are to be avoided since technical sulfonyl tends to begin freezing slightly below this temperature. If the product is to be handled as an oil, some hydrolysis will take place if frozen material is overheated during melting with water present.

Item 6. Hydrolysis of Sulfonyl During Drowning

The rate of sulfonyl hydrolysis is a direct function of the water-sulfonic interfacial area and agitation during drowning will result in considerable hydrolysis and yield loss. This effect is increased with an increase in temperature during drowning (see graph). The gentle agitation obtained by running the sulfonation mass and drowning water concurrently into the vat is sufficient to carry out the drowning and washing operation. Mechanical agitation during drowning should not be used.

Benzene [illegible]



HYDROLYSIS OF BENZENE SULFONE CHLORIDE AS A FUNCTION OF TEMPERATURE AND EXTENT OF AGITATION

FIGURE 1

Data: 3.5 parts H_2O to
1.0 parts $PhSO_2Cl$

5/13/42 RMM
4/11/44 WWF

Page 9. Operating Instructions

Approximate flow of drowning water 30-40 gallons per minute. Temperature of overflow water is not to exceed 40°C or go below 20°C.

In the study of the process as reported by Dr. Jackson,

Dr. Donald R. Jackson, A. B., Ash and K. Aoki, Material Balance Studies of the Sulfonyl Process Status Report From the Organic Department. Oct. 28, 1949.

---

the following information was noted:

Pagination C-6210

Sulfonation mass drowned in the Organic Laboratory in water 18-20°C. Oil washed in 3 portions of cold water, each 8% by volume of the oil.

Percentages

	Laboratory	Pilot Plant
Sulfonyl Chloride	91.2	91.5
Diphenyl Sulfone	7.0	6.5
Acidity as H_2SO_4	0.09	0.36
Water	1.5	1.3
Total	99.8	99.7
Sp. Gr. @ 60°F	1.365	1.365

Distillation

Sulfonyl Chloride	90.5	89.0
Diphenyl Sulfone	7.3	7.4

Charge and weight yield data:

Benzene 1919 lbs. - Acid 6,000 lbs.

	Laboratory Aliquot	Pilot Plant
Chlorosulfonation Mass		7535
Drown Mass (Technical)	2.86	3234
Pilot Plant (Sulfonyl Content)		2960
Lab. Sulfonyl Content	2.61	
Diphenyl Sulfone Content		
Pilot Plant		210 lb.
Laboratory		228 lb.

% yield data of sulfonyl chloride for run C-6210

Based on	Laboratory	Pilot Plant
Benzene	68.7	68.6
Chlorosulfonic Acid	65.4	65.5
% Diphenyl Sulfone:		
Benzene	8.9	8.2
Chlorosulfonic acid	8.5	7.8

Discussion: The yield of 68.6% based on benzene is considerably higher than the 58.7 from previous laboratory study.

Further information obtained was that the pagination sheet concerning run C-6210 showed that the drowning time required was 21.17 hours while the single redrowning required 1.83 hours. Also that the 3234 pound yield was 9.25 per cent (as based on benzene) over the average plant production yield.

Emulsions may sometimes be broken according to John C. Ware,

John C. Ware, The Chemistry of the Colloidal State. John Wiley and Sons Inc., New York City, 2nd ed. p. 246, 1936

---

by mechanical agitation or pounding; freezing; heating; centrifuging; action of electric current; addition of substances by which the protecting film is removed by chemical reaction or its effect decreased to a critical value by adsorption.

According to William Clayton

William Clayton, The Theory of Emulsions and Their Technical Treatment, P. Blakiston's and Sons and Co., Inc. Philadelphia, 3rd ed. p. 120, 1936.

Hatschek mentions the theoretical possibility of an emulsion of two liquids having the same density; such an emulsion should be quite stable.

PRIOR EXPERIENCE

In the commercial manufacture of benzene sulfonyl chloride at the Pilot Plant of the Wyandotte Chemical Corporation, technical grade benzene was directly chlorosulfonated by chlorosulfonic acid as indicated in the previous discussion. Chlorosulfonic acid was charged into a glass lined sulfonator and the benzene was added slowly with agitation and close temperature control. The benzene-chlorosulfonic acid sulfonation mass, a dark brown heavy liquid, was then drowned into a vat of water where the unreacted chlorosulfonic acid was spent and the benzene sulfonyl chloride separated as a heavy emulsion. Fresh water was supplied continuously to a drowning vat equipped with cooling coils and carried out the dissolved acids in its overflow. The benzene sulfonyl chloride emulsion layer which settled to the base of the vat and was withdrawn when the vat became about two-thirds full. The benzene sulfonyl chloride layer was then pumped up to a settling tank, settled, and then redrowned into the drowning vat. When the redrowning operation reduced the acidity to 0.25% as sulfuric acid, the benzene sulfonyl chloride emulsion was again settled and then transferred into a large storage tank. After storage the technical grade benzene sulfonyl chloride was produced by agitating the emulsion with clay, settling the mixture and then filtering the liquid layer. A 99% benzene sulfonyl chloride product was produced by distilling the settled emulsion.

In the initial drowning operation the incoming sulfonation mass stream was dispersed by the entering water flow. No type of mechanical agitation was used as it was believed that agitation would cause great hydrolysis losses. Nevertheless, the incoming sulfonation mass was agitated by the boiling action caused by the reaction of the acids and the water and by the incoming stream of water. The reaction of the chlorosulfonic acid and sulfuric acid contained in the sulfonation mass was exothermic and produced HCl gas. The gas liberated was removed by an exhaust system while the heat was removed by water cooled coils. The cooling was necessary as a temperature greater than a certain limit would produce rapid hydrolysis. Temperature control was regulated by the rate of sulfonation mass addition, and by the flow of water in the cooling coils. Thus the drowning rate was dependent upon the temperature of the water supply. A too rapid addition of sulfonation mass, even when the water was sufficiently cold to maintain a proper temperature, would cause great entrainment losses.

It was noted that entrainment losses were always present, the degree of loss depending upon the rate of water overflow and degree of suspension of benzene sulfonyl chloride globules in the waste water. With an overflow rate as per operating instructions, the entrainment losses were reduced, but the time required for drowning of one batch of sulfonation mass was twenty to thirty hours. Because of production demands and the boredom of the long tedious drowning process, the average drowning time was reduced by increasing the rate of wash water overflow. This in turn removed the produced heat faster and allowed a more rapid sulfonation mass addition while maintaining the maximum temperature limit. The entrainment losses were thus correspondingly increased.

After one-fourth of the sulfonation mass was drowned into the drowning vat, the emulsion was allowed to settle for 20 minutes, and then was pumped into an overhead settling tank. After the entire batch was drowned and pumped up to the settling tank, the emulsion was redrowned into the drowning vat. The redrowning rate was much faster than the initial drowning rate for, since the greater part of the acid was removed, the redrowning produced very little heat and caused no difficulty in temperature control. Entrainment losses were also noted in the redrowning process. The average batch required two to three redrowning operations. Average production redrowning time was about two hours. Upon reducing the acidity to the required amount, the emulsion was pumped to the settling tank to settle for two to four hours before transferring to a large storage tank. The time required for the drowning and redrowning varied from eight to twenty hours for an average production batch.

Twenty-three to thirty hours were required when the water overflow conditions were carefully controlled.

After removing water from the settled emulsion by agitation with clay in a 55 gallon drum, the clay particles were allowed to settle and the benzene sulfonyl chloride liquor was filtered to remove the suspended impurities. As performed in the pilot plant, the process was physically objectionable to the operator because of the toxic, disagreeable odors involved. The process was also very slow and uncertain. If 500 pounds of clear product could be obtained in an eight hour period the results were exceptional. On the average it required ten to fifteen hours to produce 500 pounds of product.

Market demands required the clarification of the emulsion and the removal of water was also necessary to prevent hydrolysis in shipping or when stored in tightly closed containers. Hydrolysis produced HCl which corroded metal containers and created an internal gas pressure which made drum handling and opening hazardous. The distilled product would be more economically distilled by using a charge low in water instead of the water rich emulsion.

DISCUSSION OF RELATED LITERATURE AND PRIOR EXPERIMENCE

The published literature concerning the preparation of benzene sulfonyl chloride mentioned the cause and effects of hydrolysis. Clarke stated in his notations that unless the sulfonyl chloride was removed from water as soon as possible, the yield would fall and that moisture present during distillation would promote decomposition. Wilson felt that it was the effects of colloidal droplets of benzene sulfonyl chloride in water that accelerated hydrolysis. But, as the Saccharinfabrik patent mentioned, phase separation of the sulfonation mass by the addition of water was possible without loss of yield.

The Pilot Plant reports emphasized the importance of proper temperature control and of avoiding mechanical agitation, but because of the nature of the chemicals involved, this temperature control would be difficult to do by simple batch drowning.

The apparent importance of preventing the hydrolysis of benzene sulfonyl chloride when in contact with water lead to the adoption of the drowning process without the use of mechanical agitation. It was believed that agitation greatly increased the interfacial area of the benzene sulfonyl chloride and thus increased the hydrolysis losses. But in the drowning process devised by the pilot plant of the Wyandotte Chemicals Corporation, it appeared that average production entrainment losses greatly offset any saving that might have been brought about by not using mechanical agitation.

When operated under exacting conditions, the yield of the pilot plant process compared favorably with the corresponding laboratory yield, but the operation cycle time required was prohibitive to commercial production. The yield of the carefully controlled operation was 9.25% greater than the average stated yield which indicated that at least 400 pounds of benzene sulfonyl chloride were lost at each batch drowning. The actual average losses were probably 600 to 800 pounds per batch.

The clarification process for obtaining the clear technical benzene sulfonyl chloride was entirely unsatisfactory and it was apparent that a more suitable means must be devised to break the benzene-sulfonyl chloride emulsion.

The need for improvement of the present pilot plant process of manufacture of benzene sulfonyl chloride was demanded if any type of commercial production, even on a small scale, was to be attempted. The man-hours of labor required per batch of benzene sulfonyl chloride was prohibitive on the basis of labor cost per pound of finished product. When one considered the equipment withdrawn from production for the long cycle time required, the cost in terms of lost production and inefficient utilization of manpower warranted immediate correction. It was also obvious that prevention of the occurring entrainment losses would considerably increase the yield of product.

Undoubtedly minor improvements and additions to the equipment used would tend to increase efficiency of the pilot plant process; but in order to enter into commercial production, a really economical and efficient method would have to be devised.

CHAPTER III

EQUIPMENT AND PROCEDURE

EQUIPMENT

All experimental work on phase separation of the sulfonation mass and extraction of acids from the benzene sulfonyl chloride emulsion was performed using the apparatus as shown in figure 2. During the trials some slight modifications of the apparatus were made as described in the procedures for the various trials.

The equipment used for the experimental trials was improvised from pieces of equipment available in the laboratory.

A glass stopcock and 10 mm. glass stem were attached to a 2 liter pyrex beaker to serve as a storage container for the benzene-chlorosulfonic acid sulfonation mass.

Another glass 2 liter pyrex beaker had a short piece of 16 mm glass tube attached to serve as an overflow exit at about the midpoint of the side of the beaker. A piece of 8 mm glass tubing was attached on the opposite side of the beaker at a point about 2 inches from the top to act as the inlet for water. This beaker was used as the drowning container.

1/2" lead tubing from a carboy pump was coiled and placed in the drowning container to serve as a cooling coil. Lead was chosen as a material so that industrial material contact conditions were simulated. An electric agitator was used in the drowning container.

A four-foot, 2.75 inch O.D., glass pipe was fitted with a 16 mm glass tube overflow five inches below the top. Number 13½ rubber stoppers were used on each end of the tube.

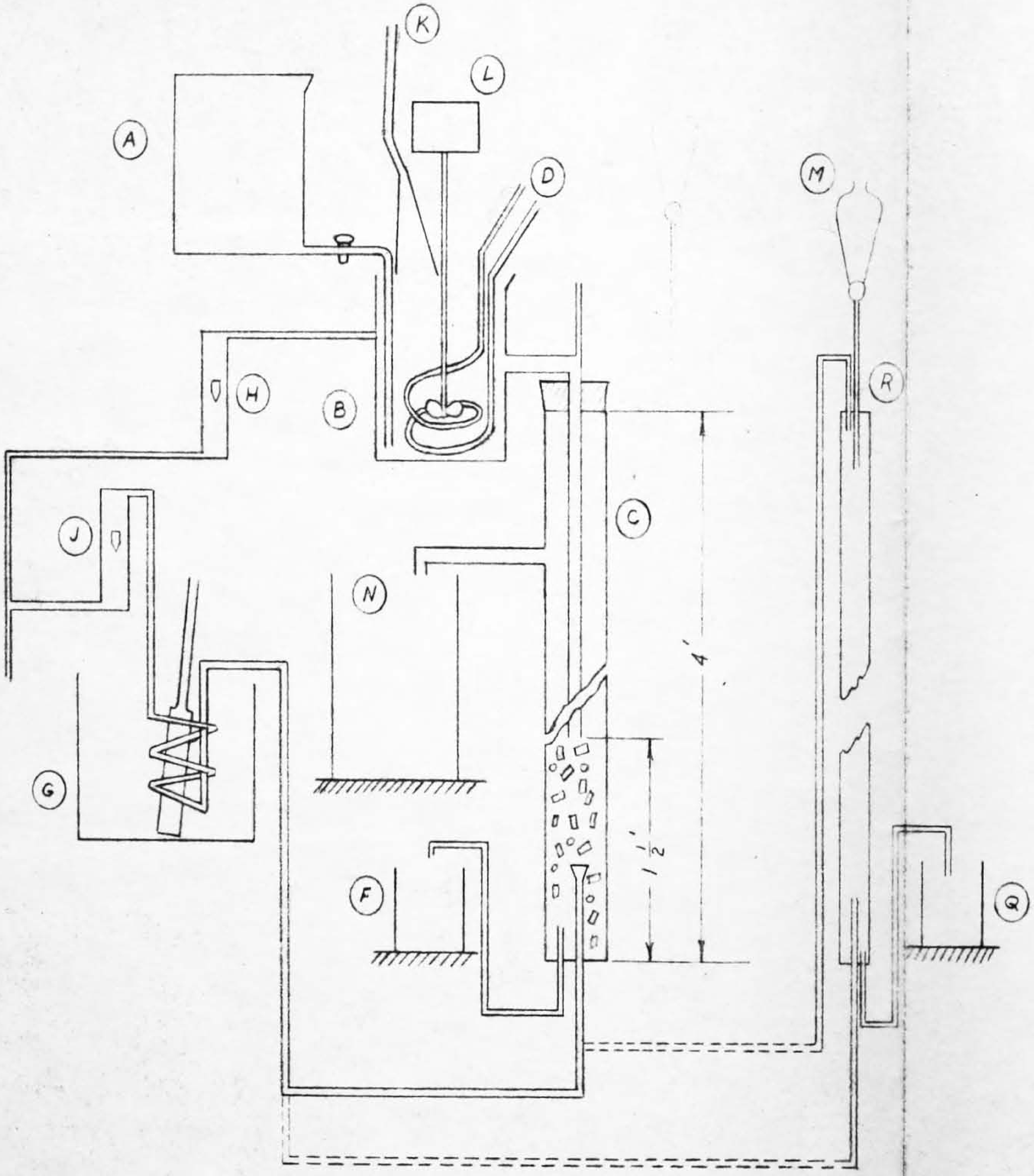
The delivery tubes to the column was made from 16 mm glass tubing and extended 2.5 feet into the column. A piece of 6 mm glass tubing was attached to the delivery tube at the bend to act as a release for entrapped gas.

About four feet of 1/4 inch copper tubing was coiled and placed in a hot water bath in order to warm the water supplied to the column. The water was warmed because the tap was seasonally cold and it was the desire to reproduce normal conditions.

An auxiliary extraction column was made from 3 feet of one inch glass pipe. The pipe was packed with broken raschig rings. A separatory funnel served as a supply container to the column.

Rotometers were used on the water inlets to control the flow of water.

FIG. 2 SKETCH OF APPARATUS USED



KEY TO SKETCH OF EQUIPMENT

A SULFONATION MASS CONTAINER

B DROWNING CONTAINER

C EXTRACTION COLUMN $2\frac{3}{4}$" DIA.

D LEAD COOLING COILS

F PRODUCT CONTAINER

G HOT WATER BATH

H DROWNING WATER ROTAMETER

J WASH WATER ROTAMETER

K FUME EJECTOR

L MOTOR DRIVEN AGITATOR

M EMULSION CONTAINER

N WASTE WATER CONTAINER

Q PRODUCT CONTAINER

R EXTRACTION COLUMN 1" DIA.

UNIVERSITY OF DETROIT
COLLEGE OF ENGINEERING
DETROIT MICHIGAN

TITLE REFINING OF $C_6H_5SO_2Cl$
SCALE NONE
DATE 5-12-50
DRAWN BY E. GACH J. BOCHINSKI

The weighings were made on a Toledo Balance with a 30 lb limit with 1/100 lb graduation.

PROCEDURE

With a reference to figure 2, the procedure for trials A, C, D, E and K was as follows: The sulfonation mass was stored in calibrated container A. The drowning container B and column C were filled with water before any sulfonation mass was charged. The drowning water and the sulfonation mass were fed into the drowning container B with agitation rapid enough to prevent the benzene sulfonyl chloride from settling. The drowning water rate was adjusted so the rate at which the sulfonation mass was fed in was controlled by the temperature rise in the drowning beaker. Thus a constant feed rate was established. As the mixture in the drowning container over-flowed into the extraction column C the column wash water was adjusted so that negligible entrainment resulted. The product was withdrawn into container F. When steady state conditions were apparent, initial readings on sulfonation mass and wash water containers were recorded and the emulsion level in the column was brought to a definite point.

The measurements which were recorded are those listed in the data sheets. Specific gravity was determined by a hydrometer. Sulfonation mass density was determined by weighing a definite volume in a 100 cc graduated cylinder on a balance.

Trials A and C were performed using marbles as packing in the counter current extraction system. A measurement was made of the sulfonation mass charged, the wash overflow, and the collected producted.

In trials A and C the equipment was assembled as in sketch No. 2. The wash water passed directly from the heating coils to the base of column C. The packing used in column C was 5/8" marbles packed to within 2" of the delivery tube. A wad of glass wool packing was placed near the exit of the column to prevent globules of benzene sulfonyl chloride from being carried out by attached gas bubbles.

Trial B was performed by dropping the sulfonation mass into a large beaker with rapid agitation and then allowing the mixture to settle for 40 minutes. With this method there was no possible overflow loss; it was essentially an equilibrium batch extraction. The layers were decanted and measured.

In trials D and E the equipment was the same as in trials A and C except that 1/2" raschig rings were used as column packing, which extended to about 4" above the end of the delivery tube. The agitation in the drowning vat was regulated so that it was just fast enough to keep the benzene sulfonyl chloride from settling in the drowning container.

In trial F the drowning container B was disconnected from the extraction column. Water entered the container. after passing through rotometer H and overflowed slowly through the container exit. The cooling coils were operated at the same rate as trials D and E. No agitation was used. The following were observed for trial F: time of run, temperature, sulfonation mass charged, overflow collected, and the amount of lost produce in overflow.

In trial K the equipment was enlarged by attaching the auxiliary extraction column as shown in figure 2, so that the effective extraction column length was increased. The procedure during this trial was essentially the same as in trials D and E except that the emulsion layer from the column C was continuously transferred by beaker to container M. The valve in container M was so regulated that it permitted the same rate of flow as the flow of the product from the bottom from column C.

In trial K-K the apparatus used is described in figure 3. The container was first filled with water and then a water jet delivered the wash water so that the mass entering the container was dispersed as in the pilot plant.

method. At intervals of time during during the run, temperatures were observed in the various zones during the drowning operation. The following measurements were also taken: Volume of sulfonation mass charged, weight of overflow water, volume of emulsion remaining in drowning vat.

The titration procedure was as follows: A 5 ml sample of the emulsion, withdrawn with a pipette, was mixed with 50 ml of carbontetrachloride and 25 ml of water. Four drops of methyl orange were used as indicator. An approximately 1/10 normal NaOH solution was slowly titrated into the agitated mixture until an end point was reached that persisted for 3 minutes or more.

The apparatus used during experimental work on the breaking of the benzene-sulfonyl chloride emulsion was a batch centrifuge of the International Equipment Company, size 1, Type SB; a 500 ml glass bottle attached to a manometer and a laboratory aspirator.

In the clarification trials by centrifuging, 50cc samples of the emulsion were placed in glass containers in the centrifuge. The emulsion being centrifuged were checked for clarity at intervals of time. The clarification time and acidity were recorded for samples of varying acidity.

In the clarification trials by low pressure, low temperature distillation of water, 25 cc of emulsion were pipetted into a clean, dry, 500 ml glass bottle and the pressure was reduced by means of a water aspirator. Trials were run with and without agitation. The time and vacuum needed for clarifying the emulsion was recorded. The clarified emulsions were withdrawn and the volume measured again with the pipette.

In the clarification trials using a continuous process, column R (fig. 2) was evacuated by means of a small laboratory type water aspirator attached by means of a pressure hose to the outlet at top of column. After the system was evacuated and dry, the benzene sulfonyl chloride emulsion was fed into the column from container M. The condition of the liquid was observed as it settled on the bottom of the column.

CHAPTER IV

DATA AND OBSERVATIONS

TRIAL A DATA

Performed April 6, 1950. Sulfonation mass used was manufactured November 9, 1949, Wyandotte Research pagination number C-6361-B-1. The sulfonation mass was charged into the drowning vat until steady conditions were reached. A mark was made near the base of the extraction column and the sulfonyl collected was withdrawn to this mark. The drowning container agitation was rapid.

Recorded Readings:

	Initial	Steady State	End of Run
Rotometer H	35	35	35
Rotometer J	30	30	30
Temperature in drowning beaker	35	35	35
Sulfonation mass scale reading	7.9	6.5	2.6

Volume emulsion collected during steady state 345 cc

Wash water collected during steady state conditions 10.11 lbs

5/8" marbles stacked to 2" below feed point in column C were used as packing.

Density of sulfonation mass 1.55 gm/cc

TRIAL B DATA

Performed April 6, 1950. The sulfonation mass used was the same as in trial A.

In this trial the sulfonation mass was drowned into a known amount of water in a large beaker while being agitated by a motor driven agitator. No cooling coils were used. The purpose of this trial was to determine what amount of sulfonyl would be produced by equilibrium batch drowning.

Water placed in beaker	5.64 lbs
Mass charged	300 cc
Sulfonyl layer collected	145 cc
Acidity of sulfonyl	0.2 %

Temperature did not rise over 35° during drowning. After addition of sulfonation mass the agitation was stopped and the mixture was allowed to settle for 40 minutes. The water layer remained turbid. It was noted that after long standing the wash water sample saved separated into a clear liquid and a white, cotton-like, mat.

TRIAL C DATA

Performed April 6, 1950. The sulfonation mass used was the same as in trial A. Time was recorded after system reached steady state conditions. 5/8" marbles were used as packing in column C.

Recorded Readings;

Time in minutes	0	6;05
Rotometer H	35	35
Rotometer J	30	30
Temperature in drowning beaker	35	35
Sulfonation mass scaler reading	7.2	2.45

Benzene sulfonyl chloride emulsion collected during steady state conditions 420 cc

Waste water collected during steady state conditions 11.89 lbs

Acidity 0.24% as sulfuric acid

TRIAL D DATA

Performed April 11, 1950. Sulfonation mass pagination No. C-6364-A used was manufactured at Wyandotte Chemicals. 1/2" raschig rings were used as column packing which extended to about 4" above the end of the delivery tube. The agitation in the drowning vat was just fast enough to keep any benzene sulfonyl chloride from settling in the drowning container.

<u>Recorded Readings</u>

Time in Minutes	0	5	5:30	13:30
Rotometer H	50	50	50	50
Rotometer J	13	13	13	13
Temperature in drowning beaker °C	10°	35	35	35
Sulfonation Mass Scale Reading	9.9	7.25	6.9	1.65

Volume emulsion collected during steady state	443 cc
Wash water collected during steady state conditions	11.42 lbs
Temperature of wash water collected	30°C
System reached steady state conditions after 5 minutes	
Acidity of the emulsion	0.76%
Density of sulfonation mass	1.55 gm/cc

TRIAL E DATA

Performed April 11, 1950. The same sulfonation mass was used as in trial E. 1/2" raschig rings were used as column packing which extend to about 4" above the end of the delivery tube. The agitation was just fast enough to prevent the emulsion from settling.

Recorded Readings:

Time in Minutes	0	3	11.25
Rotometer H	26	27	27
Rotometer J	30	31	31
Temperature in drowning beaker °C	13	35	30
Sulfonation mass scale reading	7.9	5.9	1.5

Recording time interval	3 to 11:25 minutes
Volume emulsion collected during steady state conditions	345 cc
Wash water collected during steady state conditions	12.38 lbs
Wash water temperature	30°C
Emulsion acidity	0.06%
Specific Gravity of emulsion	1.36
Density of sulfonation mass	1.55 gm/cc

System reached steady state conditions after 3 minutes

Acidity of emulsion 8.06% as sulfuric acid.

TRIAL F DATA

Performed April 11, 1950. The sulfonation mass used was the same as in trial E.

This trial was performed in a manner which was similar to the method used in the Wyandotte Pilot Plant. This was done to obtain some type of comparison to the methods used so that efficiencies could be compared.

The drowning container B was disconnected from the extraction column. Water entered the container after passing through rotometer H and overflowed slowly through the container exit. The cooling coils were operated at the same rate as in trials D and E. No agitation was used.

Recorded Readings:

Time in Minutes	0	2:30	8
Rotometer H	30	30	30
Temperature	17	20	
Mass Reading	5.65	5.1	4.65
Overflow collected			2.80 lbs
Sulfonyl in overflow			15 cc

Acidity of sulfonyl in drowning container very high

The entire contents of the drowning container when mixed with the entire overflow and weighed was 4.0 lbs. The total sulfonyl layer then decanted was 74 cc or approximately 0.22 lbs.

TRIAL J DATA

Clarification by batch centrifuging. Performed April 12, 1950. 50 cc samples were placed in graduated glass containers in the centrifuge. The speed of the centrifuge corresponded to a rheostat setting of 11. The conditions of the emulsions were observed at intervals. Samples from trial A, C, D, and E were centrifuged.

Sample A (acidity of 0,43% as sulfuric acid)
After one hour no effect on the emulsion

Sample C (Acidity of 0.24% as sulfuric acid)
After one hour the samples were still cloudy although a slight change in emulsion density was observed. The emulsion appeared more dense in the upper zone.

Sample D (acidity of 0.7% as sulfuric acid)
After one hour absolutely no shifting of the emulsion layer occurred.

Sample E (acidity of 0.06% as sulfuric acid)
After three minutes the sample was only very slightly cloudy.
After 6 minutes of centrifuging the sample was clear with no visible water dispersion.

TRIAL K DATA

Performed April 15, 1950. The sulfonation mass used was freshly prepared on the same day by Wyandotte Pilot Plant. The second packed column R was put in series with column C to obtain a greater washing effect. The emulsion from column C was transferred to container M by means of a beaker. The flow of the emulsion from container M was about the same as the flow of emulsion from column C. The sulfonation mass which was charged was weighed prior to beginning of the trial.

<u>Recorded Readings:</u>

Recording interval, minutes	0	52
Rotometer H	23	23
Rotometer J	20	20
Temperature in drowning beaker ^{o}C	35	35

Sulfonation mass charged during trial interval 13.13 lbs.

Benzene sulfonyl chloride recovered during trial interval 5.79 lbs

Steady state conditions were reached before zero time recording

Acidity of emulsion 0.7% as sulfuric acid

Specific gravity of emulsion 1.36

TRIAL KK DATA

The pilot plant method was simulated in this trial using the same sulfonation mass as used in trial K. The drowning container was disconnected from the system and connected as indicated in sketch #3. A water jet delivered the water used so that the mass entering the container was dispersed as in the pilot plant method. During the operation of the trial four definite zones were noted in the container (these zones were also present in the pilot plant operation). The upper overflowing zone was a clear waste liquid which contained a few droplets of benzene sulfonyl chloride, this was designated on the sketch as zone A. A second zone, zone B, was composed of a turbid liquid probably containing fine droplets of sulfonyl. The third zone, interfacial zone C, was the contact zone between the sulfonyl emulsion phase and the water-acid solution phase. Signs of reaction were noted at the interface; this was due, undoubtedly, to the high acidity of the sulfonyl layer.

Recorded Readings:

Date	April 17, 1950
Rotometer reading	30
Mass charged	1.01 lbs.
Overflow collected	6.94 lbs.
Sulfonyl in overflow	25 cc or 0.075 lbs
Sulfonyl in drowning container	120 cc or .360 lbs

Total sulfonyl obtained 145 cc or .435 lbs

Acidity of sulfonyl in drowning container

3.28% as H_2SO_4

Sulfonyl collected less 3% acid = 0.35 lbs.

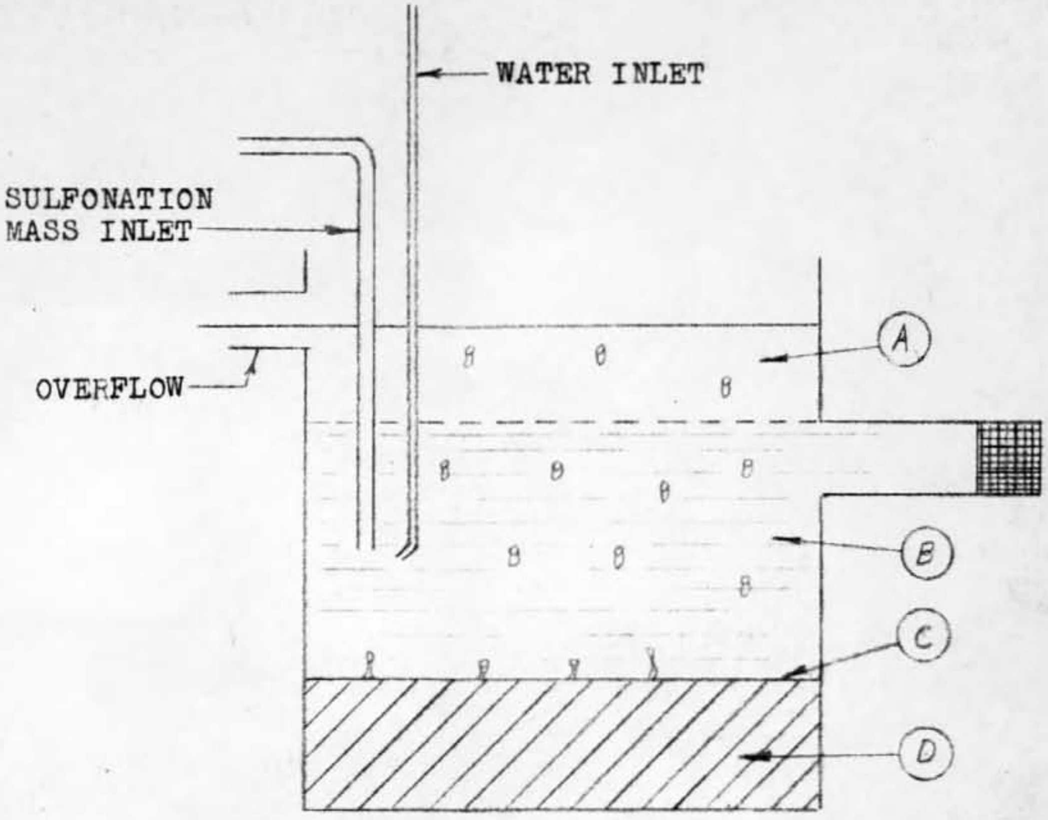
The following temperatures were recorded:

Interval Recorded	Zone A °C	Zone B	Zone C	Zone D
1 - 2 min.	22	27	37.5	--
3 - 4 min.	28.5	30.5	38	--
7 - 8 min.	26	26.5	38	--
15-16 min.	30	30	38	37

Total trial time 17:25 minutes.

The definite difference in the drowning container demonstrated what the investigators had suspected. The thermocouple bulb as placed in the pilot plant drowning vat would not give a true maximum temperature reading if it were not at the layer interface. Thus since the contents were not agitated, the temperature of certain zones must have at times greatly exceeded the allowable temperature limit and thus caused hydrolysis losses. Since some globules were carried to the water surface by gas bubbles, it was impossible to prevent the loss of product with the waste water.

FIG.3 APPARATUS AND CONDITIONS FOR TRIAL K-K



CONTAINER B AS DETACHED FROM APPARATUS IN FIG 2

KEY:

A CLEAR ZONE SOME $PhSO_2Cl$ FLOATING ON SURFACE

B CLOUDY ZONE $PhSO_2Cl$ DISPERSED IN WATER

C INTERFACIAL ZONE. BOILING ACTION TOOK PLACE WITH HCl GAS BUBBLES CARRYING OFF $PhSO_2Cl$

D EMULSION ZONE. WATER APPEARED TO BE DISPERSED IN CONTINUOUS $PhSO_2Cl$ PHASE.

REFINING OF $PhSO_2Cl$
THESIS CHE 196 a 5/12/50
E. GACH J. BOCHINSKI

CHEMICAL ANALYSIS DATA

The following samples were submitted to the Pilot Plant laboratory for analysis;

Sample No.	Description
1	Sulfonation mass, C-6364-A, used in Trials D, E, and F
2	Sulfonation mass, C-7392, used in Trials K and K-K
3	Emulsion obtained from Trial D
4	Emulsion obtained from Trial E
5	Emulsion obtained from Trial K

Chemical Analysis reported May 10, 1950

Sample No.	% $phSO_2Cl$	% Free Acid as H_2SO_4	Water %	$phSO_2ph$ %
1	39.1	53.9		
2	40.7	54.4		
3	83.8	0.60	1.70	7.17
4	81.0	1.16	4.00	7.13
5	85.2	1.3		

TRIAL L DATA

Clarification by batch centrifuging. The same procedure was used as in trial J. A portion of the emulsion layer from trial K was rewashed twice before centrifuging. The acidity was negligible as indicated by methyl orange. After rewashing the sample was settled for one hour before centrifuging. 20 minutes of centrifuging at rheostat setting of 11 were required to clarify the emulsion. After settling for 36 hours only 8 minutes were required to clarify the emulsion.

TRIAL M-1 DATA

Clarification by low temperature vacuum batch distillation. Performed April 19, 1950. Rewashed emulsion from trial K was used in this run. Acidity was negligible as indicated by methyl orange. 25 cc of emulsion at 25°C were measured with a pipette and placed into a dry 500 cc bottle. The pressure was reduced to about 15 mm for 20 minutes before the emulsion became clear. The liquid was withdrawn and measured in a pipette. No significant losses were observed.

TRIAL M-2 DATA

Clarification by low temperature vacuum batch distillation. Performed April 19, 1950. The same emulsion and procedure were used as in trial M-1 except the rapid agitation was supplied by shaking the bottle. Temperature of emulsion was 25°C. 5 minutes were required to clarify the solution. No significant losses were observed.

TRIAL M-3 DATA

Clarification by low temperature vacuum batch distillation. Performed April 19, 1950. Same procedure was used as in trial M-1 except that rapid agitation was supplied. Material used was the emulsion from trial K. At the end of 3-1/2 minutes the liquid was clear.

TRIAL M-4 DATA

Clarification by continuous low temperature distillation. The column R was packed with broken raschig rings. The system was dried and evacuated. The pressure was maintained at 15 mm throughout the run. The emulsion was introduced at a slow rate. Temperature of feed was 30°C. The liquid was clear as it accumulated in the bottom of the column. No weights were recorded.

CHAPTER V

CALCULATIONS

CALCULATIONS FOR TRIAL K

Weight sulfonation mass charged:	13.13 lbs
Weight $PhSO_2Cl$ collected:	5.79 lbs

Per cent yield based on sulfonation mass charged:

$$\frac{5.79}{13.13} \times 100 = 44.1\%$$

Wash water used

Weight of waste water = 57.96 lbs

Weight of waste acids = 13.13 - 5.79 = 7.34

Weight of wash water = 57.96 - 7.34 = 50.62

Ratio of wash water and sulfonation mass charged

$$\frac{50.62}{13.13} = 3.85 \text{ lbs } H_2O/\text{lb sulfonation mass}$$

CALCULATIONS IN TRIAL K-K

Convert initial (I.R.) and final (F.R.) scale readings from sulfonation mass container by the use of conversion graph (figure 4).

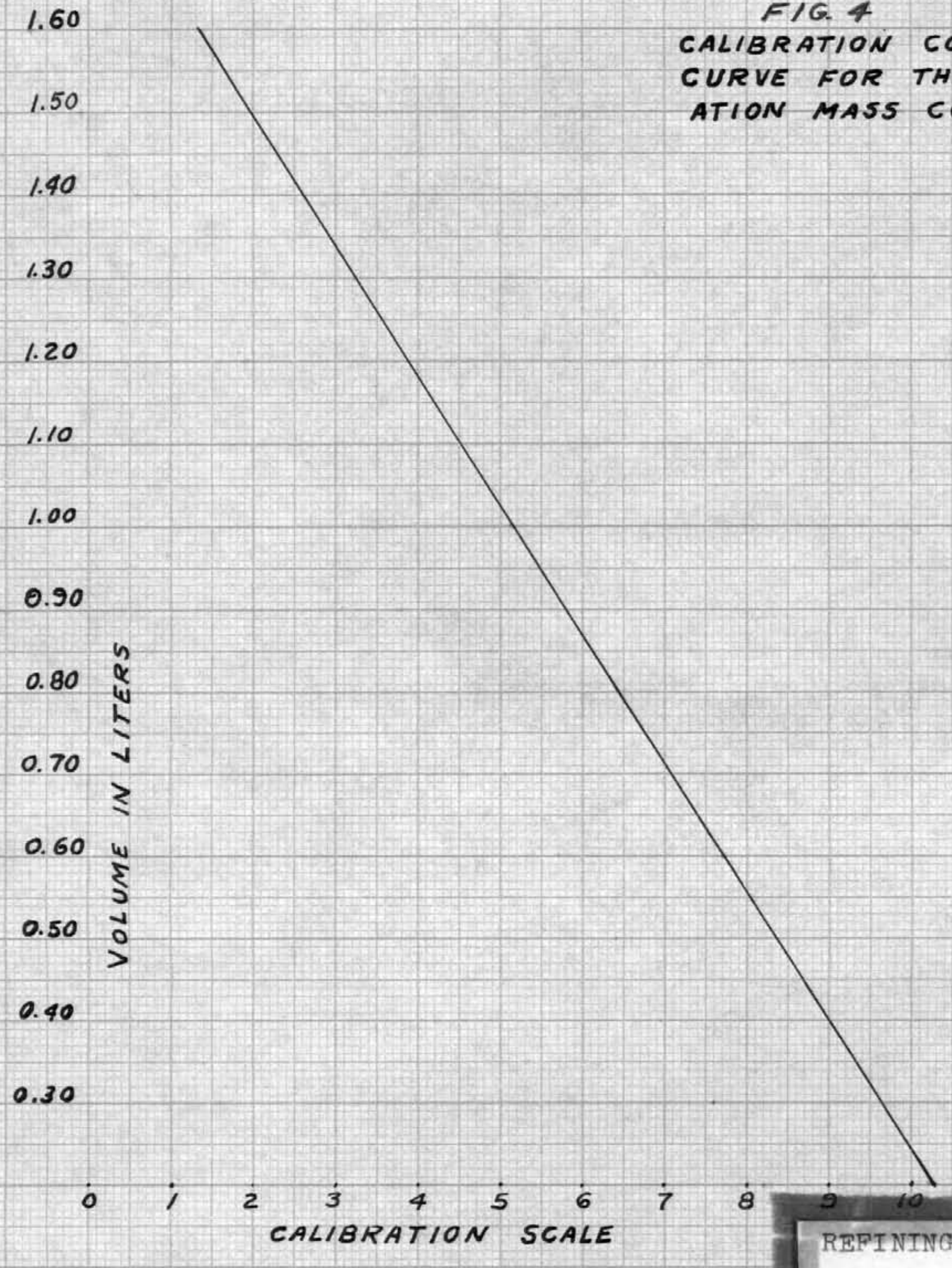


FIG. 4
CALIBRATION CONVERSION CURVE FOR THE SULFONATION MASS CONTAINER

REFINING OF $PhSO_2Cl$
THESIS CHE 196 a 5/12/50
E. GACH, J. BOCHINSKI

Weight sulfonation mass charged

F.R. = 3.8 = 1210 cc

I.R. = 5.7 = 915 cc

Net charge 295 cc

Weight $= \frac{295 \times 1.55}{453.6} =$ 1.01 lbs

Weight $PhSO_2Cl$ collected

Volume of emulsion = 145 cc

Weight emulsion $= \frac{145 \times 1.36}{453.6} =$ .435 lbs

Weight emulsion discounting entrainment

losses $= \frac{120 \times 1.36}{453.6} =$ 0.36 lbs

Weight acid in emulsion = 0.36 x .0328 = .012

Net weight of emulsion (discounting entrainment and acidity) =

.36 - .01 = 0.35 lbs

Per cent yield based on sulfonation mass charged

$100 \times \frac{0.435}{1.01} =$ 43%

Water used;

Weight waste water = 6.94 lbs

Waste acid = 1.01 - .44 = 0.57

Net water = 6.94 - 0.57 = 6.37

Water used per lb sulfonation mass charged;

$\frac{6.37}{1.01} =$ 6.31 lbs/lb

Acidity: volume NaOH = 8.25

Titration factor .077

% acid = 8.25 x 0.077 x 5 = 3.17%

CONSTRUCTION OF DUHRING LINES

The vapor pressure data for benzene sulfonyl chloride according to Hans T. Clark

---

loc. cit. p 6-8

---

was 15 mm/118-120° and 10 mm/113-115°. The vapor pressures given are for the benzene sulfonyl chloride and diphenyl sulfone mixture as recovered from the sulfonation mass.

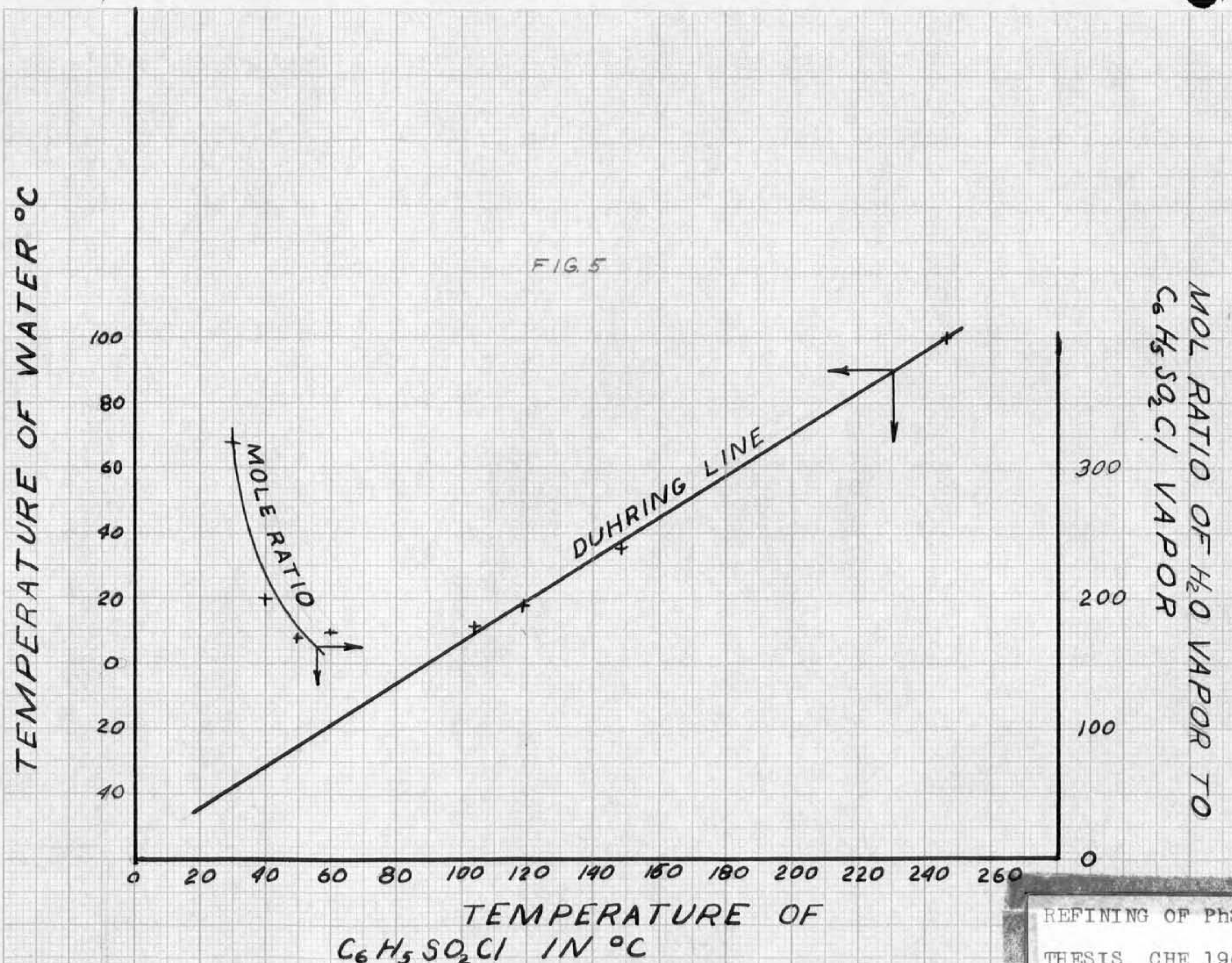
The following values were used in the construction of the Duhring Lines in figure 5.

Benzene Sulfonyl Chloride		Water	
Temp. °C	Vapor Pressure mm Hg	Temp. °C	Vapor Pressure mm Hg
246	760	100	760
118-120	15	17.6	15
113-115	10	11.2	10
148-152	40	34.2	40

The following vapor pressure relations were extrapolated from the Duhring Lines:

Temp. °C	Vapor Pressure $PhSO_2Cl$ mm Hg	Vapor Pressure H_2O mm Hg
30	0.1	31.8
40	0.28	55.3
50	0.54	92.5
60	0.85	149.4

FIG. 5



DUHRING LINES

REFINING OF $PhSO_2Cl$

THESIS CHE 196 a 5-12-50

E. GACH, J. BOCHINSKI

Vapor pressure ratios corresponding to the approximate ratios of components (water vapor and benzene sulfonyl chloride vapor) in the vapor phase was calculated for the following temperatures:

Temp. °C	Ratio H_2O to $PhSO_2Cl$
30	318
40	198
50	175
60	172

An approximation of the losses incurred during vacuum distillation of the emulsion at 30°C was made as follows:

Basis 3000 lbs

approximate water contained in emulsion	1.5%
weight water in emulsion	45 lbs
mole water per mol benzene sulfonyl chloride leaving in vapor during distillation	300

lbs sulfonyl/lb water in vapor

$$\frac{1 \times 176.6}{300 \times 18} = .0326$$

lbs sulfonyl lost $45 \times .0326 = 1.5$ lb

CHAPTER VI

STATEMENT AND DISCUSSION OF RESULTS

The results of the data were presented in the following tables:

Table I, Calculated Results of the Experimental Trials

Table II, Calculated Material Balance Based on Chemical Assay

Table III, Results of Clarification Trials

TABLE I. CALCULATED RESULTS OF THE EXPERIMENTAL TRIALS

Trial	Sulf. mass charged lbs.	$PhSO_2Cl$ emulsions collected lbs.	Water used lbs.	% yield based on sulf. mass charged	Lbs water per lb sulf. mass charged	Acidity of $PhSO_2Cl$ % H_2SO_4	Trial time in min.	Rate of drowning lbs sulf. mass per min.
A	2.105	1.033	9.04	49.2	4.3	0.42		
B	1.024	0.435	5.64	42.5	5.5	0.2		
C	2.53	1.26	10.62	49.8	4.21	0.24		
D	2.97	1.33	9.78	44.8	3.29	0.76	8;30	0.35
E	2.34	1.03	11.07	44	4.73	0.06	8;25	0.279
F	0.547	0.222* 0.169**	3.67	40.6* 30.9**	6.7		8;00	0.069
K	1313	5.79	50.62	44.1	3.85	0.07	52	0.253
K-K	1.01	0.435* 0.35 **	6.37	43 * 34.7**	6.31	3.28	17;25	0.058
Plt. Plant C-6210	7235	3234		42.9		0.36		

NOTES:

* Based on total recovery measured.

** Based on recovery of process

TABLE II. CALCULATED MATERIAL BALANCE BASED ON CHEMICAL ASSAY

Trial	Assay of Sulf. Mass % $PhSO_2Cl$	$PhSO_2Cl$ in Sulf. Mass According to Assay lbs	Emulsion Collected lbs.	Assay of Emulsion Obtained %$PhSO_2Cl$	$PhSO_2Cl$ Obtained According To Assay lbs	% Yield Obtained
D	39.1	1.16	1.33	83.8	1.11	95.7
E	39.1	0.915	1.03	81.0	0.835	91.2
K	40.7	5.35	5.79	85.2	4.93	85.1

TABLE III. RESULTS OF CLARIFICATION TRIALS

Clarification by centrifuging and distillation. A constant speed was used on all centrifuging trials.

Sample	% Acidity	% water	Centrifuging time	Distillation time
A	0.43		1 hour no effect	
C	0.24		1 hour slight effect	
D	0.7	1.7	1 hour no effect	
E	0.06	4.0	3 min. slightly cloudy 6 min. very clear	
L	negligible		20 min. very clear 8 min. very clear after solution settled for 36 hours before centrifuging	5 min. very clear
K				3.5 min. very clear

DISCUSSION OF RESULTS

Consideration of the figures in the Statements of Results as exact quantative measurement and comparison values was not warranted, because many of the assumptions made could well be questioned. But, it was permissible to use them for basing comparison on an indicative basis as the results were fairly consistant.

The yield of the experimental trials compared favorably with the results based upon Pilot Plant literature, indicating that if careful, long-period control was maintained, the entrainment losses were at a minimum and thus the resulting yields were approximately the same.

Since the yields of trials A and C exceeded trial B; D and E exceeded F; and K exceeded K-K, it was inferred that hydrolysis losses were definitely not greater when agitation was performed in limited amounts of water during phase separation. The results even indicated that hydrolysis losses may have been repressed.

The high zone temperatures noted in K-K may have increased hydrolysis losses as the total yield of K-K was less than K.

Trials showing a greater production rate indicated a greater yield.

More efficient use of water was exhibited by the obtaining of lower acid values while using a lower water ratio.

Higher yields because of less entrainment loss was indicated where a packed column and smaller volumes of water were used.

Material balances based on chemical analysis did not indicate any obvious discrepancies. The differences in acidity values as determined during the trial and by the Pilot Plant laboratory indicated that hydrolysis took place upon standing as the samples stood for quite a period of time before analysis by the Pilot Plant.

Critical examination of the results made the following disclosures.

It was assumed that the weight of HCl removed through the fume ejector was negligible in comparison to the weights recorded, thus, the weight of HCl lost was assumed negligible in the material balances.

The laboratory equipment was operated until steady state conditions were apparent and then the material balance factors were observed and recorded. It was possible that a slight excess of water and emulsion yield may have been collected in trials A and C and possibly in D and E.

The sulfonation masses used in all trials except K were not freshly prepared so an age factor may have produced misleading figures as compared to results using fresh sulfonation mass.

Error may have been introduced due to measurement errors as the volumetric measurements were converted to weight values by multiplying by the specific gravity and density conversion factors. The small amounts measured in some instances may have increased the possible experimental error. Slide rule calculations were used for all calculations as it was assumed that the accuracy of the measurements did not warrant more exacting computations.

The water source temperatures were not recorded nor was any attempt made to keep a specific temperature; it was believed that this could not introduce any significant error.

The calculations based upon chemical analysis could not be relied upon too strongly as each assay did not total 100 per cent. Also the chemical analyses were performed a long time after the particular samples were obtained

Although direct comparison of experimental and recorded results can not be applied too rigidly as the sulfonation mass of each reaction operation undoubtedly varied in analysis, it was assumed that this variation was not sufficient to prevent indicative comparison. Also, although the simulated Pilot Plant comparison trials, F and K-K, undoubtedly did not reproduce the exact pilot Plant conditions (because of the difference in the sizes of the apparatus used) indicative comparison was still assumed applicable.

During the centrifuging trials the degree of clarity was determined by visual inspection. A solution was considered acceptable when transparent and when no turbidity was observed.

The interpretations of the distillation data may be in error because the volumes of emulsions used during distillation trials were small and the data calculated from Duhring lines involved approximations and extrapolations.

CHAPTER VII

SUMMARY OF CONCLUSIONS

The results of the experimental trials and knowledge obtained through related literature and prior experience made it possible to state the following conclusions as being plausible.

In regard to mechanical agitation and its influence upon hydrolysis in the current batch and proposed industrial refinement processes, the following references were drawn:

The boiling action produced in the drowning water by the reaction of the unused chlorosulfonic and sulfuric acids in the batch process may have been sufficient to produce as much hydrolysis loss as that produced by mechanical agitation in the proposed process.

The comparatively large volumes of water used in the batch process and the subsequent hydrolysis loss may have been more than enough to offset any hydrolysis loss increase due to mechanical agitation.

The small amount of water and large amount of acid present during the phase separationmay have suppressed hydrolysis as under these conditions the sulfuric acid (about 50° Be) had the greater affinity for water.

The comparatively smaller amount of water used to wash out the acid and its more efficient utilization in the continuous extraction system tended to reduce hydrolysis losses.

The poor temperature control and localized heating as was exhibited by the batch process encouraged hydrolysis while the rapid and efficient cooling due to mechanical agitation in the proposed process prevented any higher temperature hydrolysis losses.

Since the proposed process was much more rapid, the hydrolysis losses in the batch process were greater as the contact time between water and benzene sulfonyl chloride was greater.

Concerning the entrainment losses of benzene sulfonyl chloride it can be safely inferred that due to smaller volumes of wash water overflow in the proposed process that the entrainment losses were less than in the batch process.

Also the entrainment losses were less in the proposed process as the packing served to coagulate and "wipe-out" the entrained globules of chloride.

Involving the clarification of the benzene sulfonyl chloride-water emulsion, the bulk of the turbidity producing water appeared to be removable by centrifuging.

Residual amounts of water (and even large amounts) were easily removable by low temperature vacuum distillation. This clarification process appeared much more satisfactory in all respects as compared to the clay-treating and filtering process.

As compared to the batch process, it appeared that the continuous process, when applied in industry, would mean a great saving in labor man hours; introduce more pleasant and less boring conditions; reduce the "human element" problems; reduce the requirements for rigid control and constant observation.

CHAPTER VIII

RECOMMENDATIONS

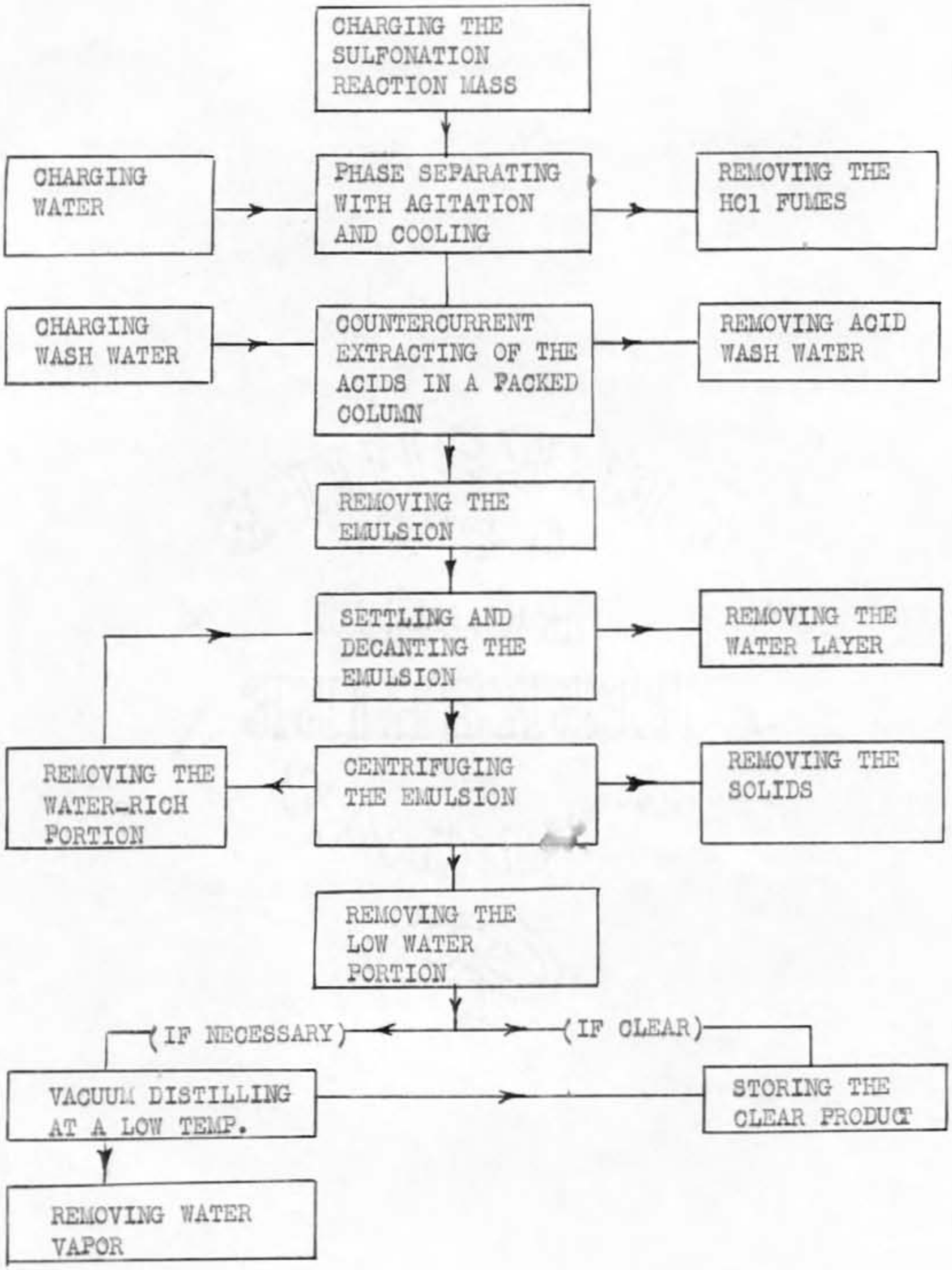
The recommendation was made that themethod of refining benzene sulfonyl chloride from benzene-chlorosulfonic acid sulfonation mass be changed to the method as indicated by the engineering flow sheet (figure 6) after further investigation substantiates the conclusions of this report.

It was also recommended that further investigation be made to determine the type and design of the phase-separating-cooling unit; the best water-sulfonation mass drowning ratio; the type and design of extraction column; thetype of packing most suitable; best extraction rates; the type of centrifuge and centrifuging factors; and the type of distillation apparatus and distillation factors.

It was advised that in order to substantiate the conclusions of our report, the equipment be enlarged to pilot plant scale, and the sulfonation mass used be freshly prepared.

FIGURE 6

PROPOSED ENGINEERING FLOW SHEET



REFINING OF $PhSO_2CL$

THESIS 196a 5-12-50

E. GACH J. BOCHINSKI