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ENGINEERING AND LABORATORY STUDIES,
POLYMER PROJECT
(Production Facilities for Boron 10)

U.S. ATOMIC ENERGY COMMISSION CONTRACT NO. AT(30-1)-1506

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by J. C. Videman TIE, date 7-7-58

THE GIRDLER CORRORATION
GAS PROCESSES DIVISION
LOUISVILLE, KENTUCKY

April 3, 1953

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I. SUMMARY AND RECOMMENDATIONS

This report summarizes the work done by The Girdler Corporation for the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1506.

It includes cost estimates, and design, engineering, procurement and construction schedules for plants to produce Boron 10 in quantities of 500 and 750 kilograms per year in concentrations of 70% and 95%. (Due to the relatively small differences in cost between plants for producing 70% and 95% Boron 10, the 80% case included in the contract letter was abandoned.)

Prospective plant sites at Lake Ontario and Middlesex, New Jersey have been evaluated, and the recommendation made that the Middlesex, New Jersey site be utilized for this project.

Process designs and plant layouts have been made for methyl ether-boron trifluoride complex preparation and fractionation and for the production of pulverized crystalline boron from fractionated complex.

Laboratory studies have been carried out on the thermal degradation of methyl ether-boron trifluoride complex and on the effect of methyl fluoride recirculation through the fractionation. Other laboratory studies included dehydration of methyl ether and corrosion tests with complex on pump and packing materials. Reports on the work appear in the Appendix.

Six cost estimates have been prepared as summarized in Table A, below:

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TABLE A

Summary of Cost Estimates

Cases	Estimated Total Cost	Capacity kg/yr.	Boron 10 Concentration	Fractionator Arrangement	
I	$1,886,445	750	95%	8-93' columns	[illegible]
II	1,640,610	750	70%	5-97' columns	485
III	1,851,680	500	95%	8-93' columns	
IV	1,615,875	500	70%	5-97' columns	
V	2,096,130	750	95%	20-42' columns	[illegible]
VI	(1,846,040) (2)	750	95%	(10-42' columns) (6-old columns(1))	

(1) Columns previously used by Standard Oil of Indiana.
(2) Cost of purchasing and reconditioning old columns and accessories not included.

These costs are based on location of the plant at Middlesex, New Jersey, where factory and office buildings are available. At a site where such facilities are not available, it would be necessary to add about $150,000 for such facilities.

Cases I through IV cover the four conditions of quantity and concentration listed above. Since there is only about 17% increase in cost for the 50% increase in capacity of Case I as compared to Case IV, we recommend that Case I be selected from these four cases. Case V is a duplicate of Case I, processwise, but with column heights reduced from 93 feet to 42 feet. This change adds 11% to the cost. We are making no recommendation between Cases I and V, since the principal choice here involves the subject of project security. In both Cases the columns would be totally enclosed. In Case I a penthouse approximately twenty feet square would project above the building to a total height of one hundred feet.

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In Case II a penthouse about twelve feet by sixty feet would project above the building to a total height of fifty feet. Case VI is a modification of Case V in which six columns from the previous operations have been combined with ten new columns of the type used in Case V. (Case V columns were chosen rather than Case I since the old columns were short ones.) It must be kept in mind that to the cost shown above for Case VI, the cost of purchasing and reconditioning these columns must be added. Since the use of this old equipment does not make possible any substantial cost savings, we recommend that it should not be used for the project at this time. Consequently, we are recommending Case I as our preferred choice, unless security considerations dictate the choice of Case V. It should be noted that Case I provides 60% more fractionation equipment than Case II, at a cost increase of only 15%. This equipment is available either to produce the design quantity of complex of design concentration, at design yield, or to produce substantially larger quantities at lower concentrations or yields.

Studies we have made on the preparation of elemental boron (metal) have resulted in recommendations that two alternate methods of preparation be investigated further; first, the production of diborane plus cracking to boron, and second, the electrolysis of KBF_4 and other salts to produce crystalline boron.

It is recommended that laboratory studies be made to investigate methods for removing HCl from the reduction tube effluent so that the unreacted BCl_3-H_2 mixture may be recycled. Alternately, it is recommended that studies be made to determine the feasibility of recirculating H_2 after HCl and BCl_3 have been removed from it if no process for removing HCl alone can be perfected.

The present laboratory program has indicated that recirculation of methyl fluoride during fractionation of methyl ether-boron trifluoride complex will permit operation at atmospheric pressure with low thermal degradation rates. It is recommended that this work be continued to evaluate this process and determine what effect the methyl fluoride exerts on the fractionation. A suitable method for removing methyl ether-boron trifluoride complex and methyl borate-boron trifluoride complex from the recirculated methyl fluoride also should be developed. In addition, further corrosion tests on proposed materials of construction should be carried out.

II DISCUSSION OF PROCESSES

A. Isotope Separation

It has been demonstrated in the past* that the B-10 and B-11 boron isotopes can be separated by fractionation of various boron compounds. The methyl ether-boron trifluoride complex (polymer) has a more favorable vapor liquid equilibria for the separation than most of the compounds tested and results in fractionation units of a practical size. For this reason, it was chosen as the agent to effect a separation of the isotopes in spite of some undesirable aspects such as ease of degradation by heat and high reactivity with water and oxygen. This section of the report deals with the preparation of light polymer for feed to the metal preparation step.

1. Feed Preparation

The polymer is prepared by combining gaseous dimethyl ether and boron trifluoride in equal mol quantities and condensing the resultant mixture. As shown on the flowsheet (Drawing F-4111-1) the ether and boron trifluoride are supplied from cylinders manifolded so that at least a day's run can be made before changing cylinders is required. To vaporize the dimethyl ether, heat is supplied to the cylinders by a warm water spray. The gases are reduced in pressure to approximately 25 psig at which pressure the flow quantities are measured and controlled by rotameters and hand valves. Since commercial ether contains a small amount of water, provision is made to dry the stream with activated alumina using a commercially available continuous unit. The two gases

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* National Nuclear Energy Series, Div. III, Vol. 5; Reports A-1975 and A-2350 through A-2370.

are joined in a mixing tee and the mixture passes directly into a water cooled condenser where the heat of reaction and latent heat of condensation is removed and the polymer condensed. The liquid polymer is collected in a small accumulator which also serves to separate any unreacted gas. The polymer is then pumped to a storage tank.

It is contemplated that this unit will operate only eight hours per day. The unit has been sized to produce sufficient feed in this time for the continuously operating distillation section. The storage tank has capacity sufficient for approximately one-week operation of the plant.

2. Fractionation of Polymer

a. Methods of Operation

In the fractionation of the methyl ether-boron trifluoride polymer, degradation to the borate complex and methyl fluoride is a complicating factor. A high percentage of degradation based upon the feed can probably be tolerated without destroying the efficiency of the column, since the degradation products boil considerably below the polymer and consequently concentrate only in the top few plates. However, if the degradation rate becomes too high, the borate complex could become very concentrated throughout the column. Since no data are available on the relative volatility obtainable with the borate complex, it appears desirable for the present to base the design on a low degradation rate.

Three methods of operation have been considered:

(1) Distillation at atmospheric pressure

(2) Distillation at atmospheric pressure with circulation of a diluent stripping gas to reduce vaporization temperatures.

(3) Distillation at reduced pressure.

Distillation at atmospheric pressure is attractive because of its freedom from the leakage problems associated with distillation at reduced pressure, and because the increased vapor density will permit the use of smaller equipment. Laboratory data on the thermal degradation rate of polymer refluxing at atmospheric pressure indicated that the degradation rate would be low enough (6 to 7% per day) to permit satisfactory operation. However, fractionation tests at atmospheric pressure in both glass and metal equipment gave thermal degradation rates of 30 to 50% per day, depending upon boil-up rates. The difference between the rates found in the refluxing tests and the fractionation tests is considered due to the removal of methyl borate complex from the liquid in the kettle by the fractionation column. Since these degradation rates were so high that all the feed would be converted to methyl borate complex, further consideration of fractionation at atmospheric pressure was abandoned.

By distilling at atmospheric pressure with circulation of an inert gas the temperature in the column may be kept low enough to limit the amount of degradation since the inert gas can be made to lower the partial pressure of the vapor in the column to any desired point. Since leakage of water or air into the system is undesirable, atmospheric pressure operation with a diluent is attractive from an operational standpoint.

As a diluent for atmospheric pressure operation any inert gas could be used, but it appears convenient in this case to use methyl fluoride which is one of the products of polymer degradation which always takes place to some extent in the column. Since the methyl fluoride is recycled in the system, once a quantity has built up in the system the continuous polymer degradation is sufficient to maintain the operation. The methyl fluoride needed can be obtained by high polymer degradation rates during startup or by letting it build up gradually and using an inert gas such as nitrogen for startup. The fact that methyl fluoride is a product of polymer degradation is an added reason for using it as the diluent gas, since laboratory fractionation tests have indicated that its presence in the system appears to lower the degradation rate more than can be accounted for by the temperature lowering alone. It appears to exert a repressing action on the degradation.

The estimates have been prepared on the basis of operation at atmospheric pressure with circulation of methyl fluoride because of the advantages of this operation over reduced pressure. However, equipment sized for atmospheric pressure operation with diluent gas will be suitable in size for operating under reduced pressure.

The fractionation requires a relatively large number of theoretical plates. Because of height limitations this means that a number of column sections must be operated in series to give the desired separation. Operated in this manner as a single fractionating column, the vapor from the top of a column must be transferred to the base of the preceding column and the liquid from the bottom of a column must be transferred to the top of the following column so that continuous countercurrent flow of the vapor and liquid is obtained.

Because the pressure drop through the system is cumulative and is more than can be tolerated at the condition of operation, some means is necessary to overcome it. One method is to condense the vapor at the top and reboil it at the bottom of each column using a liquid transfer pump to overcome the pressure drop between columns. Another method is to use blowers on the overhead vapor from each column to recover the pressure loss. Both methods have been operated commercially. If a recycled inert gas is used in the fractionator, the second method employing blowers is indicated. If vacuum operation is used, either method is applicable.

Where condensation of the vapor between columns is used, it is possible to effect some overall reduction in tower volume by reducing the reflux ratio in the column sections nearer the bottom reboiler. This will result in some reduction in investment. If expensive tower packing is used this procedure should be given some consideration, but if a relatively inexpensive packing is used, as presently contemplated, the operating and structural convenience of having all column sections the same size is more important.

The advantages of atmospheric pressure operation with methyl fluoride recycle as compared with vacuum operation are as follows:

(1) Atmospheric pressure operation minimizes the possibility of leakage either in or out of the system, and permits the use of regular packed valves rather than special diaphragm type valves.

(2) The liquid entering the pump suction will be well below its boiling point, and so will not be subject to troubles due to flashing. For example, with an inert gas content of 69% in the system, corresponding to a polymer partial pressure of 300 mm. of mercury at the base of the columns, the liquid will be at 222°F, while its boiling point at the pressure present in the pump suction line is about 270°F.

(3) It has been indicated by laboratory tests that the recirculation of methyl fluoride tends to repress the degradation rate of the polymer to methyl borate complex and methyl fluoride.

(4) It has been shown that methyl borate complex maintains isotopic equilibrium while passing through a fractionating column. In a multi-column fractionation unit operating under vacuum, with vacuum being maintained at the top of each column some methyl borate complex and polymer vapor will pass out through the vacuum system and be lost from each column. This vapor will have the isotopic concentration present at the top of the column from which it is lost. In atmospheric pressure operation with methyl fluoride recycle, the composition of the methyl borate complex and polymer vapors leaving the system will have the same isotopic concentration as the overhead by-product, and so will represent no added loss of desired material (The same is true of a vacuum fractionation operated with blowers to move the vapors from column to column without intermediate condensation).

(5) Sampling of gases or liquids is much easier at atmospheric pressure than under vacuum.

Operation at atmospheric pressure with methyl fluoride recycle has been tentatively chosen over vacuum operation. It is thought that the operational advantages over vacuum operation justify the choice even though vacuum operation has been demonstrated as workable on a large scale. There are some uncertainties such as the effect of the diluent on the HETP and the method to be used for purifying the recycle methyl fluoride which require laboratory investigation before a firm design can be made. Actually, the design conditions have been made such that most of the equipment specified can be used either for vacuum operation or atmospheric operation with diluent. The main differences equipmentwise are the steam jet vacuum system in the one case and the methyl fluoride purification system in the other.

b. Choice of Packing

Stedman packing was used in the columns employed in the previous plant. The nature of this packing necessitated great care in manufacture and installation to avoid bypassing. Hexagonal columns were used in the 12" and 18" sizes, which required special fabrication and machining. Tests made at that time with McMahon packing indicated that this material could be substituted satisfactorily for Stedman packing.

Another packing with HETP and capacity characteristics similar to McMahon packing is protruded metal packing, which has been developed since the previous fractionation work on polymer was carried out. This packing is less expensive than McMahon packing ($385 per cubic foot as compared with $508 for McMahon packing), and has another advantage in that it does not lose shreds of wire, as is the case with the

McMahon packing, which is fabricated from small pieces of fine wire screen. After a study of literature references available on the performance of protruded metal packing (.24" x .24"), it was concluded that this packing could be substituted satisfactorily for Stedman packing.

A comparison of the properties of .24" x .24" protruded metal packing, 1" x 1" protruded metal Raschig rings, 1" x 1" ceramic Raschig rings, 1" ceramic Berl saddles, and 1" ceramic Intalox saddles was found in the thesis of John F. Ryan, Pennsylvania State College, January, 1953, which reported results of tests made with these packings in a 12" diameter column distilling methylcyclohexane-normal heptane mixture at atmospheric pressure. Further information on the properties of the 1" ceramic Intalox saddles was found in the book "Tower Packings and Packed Tower Design", by Max Leva, published in 1951 by the United States Stoneware Company.

A study of these references indicated that the 1" Intalox saddles would have certain advantages over the .24" x .24" protruded metal packing. The flooding velocity of the 1" Intalox saddles with methylcyclohexane-normal heptane at atmospheric pressure was reported by Ryan as 3.4 ft. per second, while he found 1.65 feet per second with the .24" x .24" protruded metal packing. Thus, the throughput capacity of the 1" Intalox saddles was 2.06 times that of the protruded metal packing. Taking 3" as the HETP for the protruded metal packing, and 14" as the HETP for the 1" Intalox saddles, the relative packing volume required for the 1" Intalox saddles was 2.27 times that of the

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protruded metal. However, since the cost of the two packings is $7.50 and $350 (500 cu.ft. or more) per cubic foot, respectively, the packing required with 1" Intalox saddles will cost only 5% as much as the protruded metal packing. The increased packing volume with the 1" Intalox saddles will more than double the cost of the columns themselves, but this increase will still be substantially less than the cost of the protruded metal packing would be.

only if $/ft² and $/ft are equal

Holdup of liquid on the packing is an item of concern because of the degradation of the polymer. The holdup with the 1" Intalox saddles will be between 1/3 and 1/2 that with the protruded metal packing so that the total holdup of the system should be no greater.

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The stability of chemical stoneware packing in the presence of the polymer has been considered, and it has been concluded that no difficulty will be encountered. During the previous operation gage glasses and glass rotameter tubes were used successfully in contact with polymer liquid and vapor, while during the previous laboratory work a column packed with ceramic Raschig rings was used, many tests were made in glass apparatus, and stability tests were made with glazed and unglazed porcelain. During the present laboratory program much work has been done in glass equipment, and a stability test has been made on 1" chemical stoneware Intalox saddles. There has been no evidence reported of any deterioration of glass or ceramic material in any of the work listed above.

The pressure drop through the system should not be substantially higher with the 1" Intalox saddles than it would be with the

.24" x .24" protruded metal packing. Ryan reported the pressure drop for the protruded packing at a vapor velocity of 1.7 ft. per second to be the same per HETP as it was with 1" Intalox saddles at a vapor velocity of 2.5 ft. per second.

c. Calculation of Number of Theoretical Plates

The separation of the boron isotopes as methyl ether - boron trifluoride has been carried out in the laboratory and also on a plant scale. The data indicate that a relative volatility of 1.016 can be expected under vacuum conditions. Using this value a number of fractionation calculations were made using a modification* of Lewis's method for columns having a large number of theoretical plates. The usual simplifying assumptions were made in these calculations and in addition it was assumed that the feed entered as a liquid at the boiling point. The theoretical plates required at an infinite reflux were determined by the Fenske equation and the minimum reflux was calculated from the slope of the operating line when intersecting the equilibrium curve at the feed composition. These calculations are summarized in Figure I where the number of plates is plotted versus the reflux ratio. Three different separations are shown; 95% bottom - 95% top, 70% bottom - 95% top, and 95% bottom - 90% top. (95% bottom, 95% top, refers to 95% B 10 in the bottoms product and 95% B 11 in the overhead product).

In Figure I it is seen that increasing the overhead product composition from 90 to 95% results in 25% increase in the number of

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* B. F. Dodge and J. R. Hoffman, Industrial and Engineering Chemistry, Vol. 29, p. 1434, Dec. 1937.

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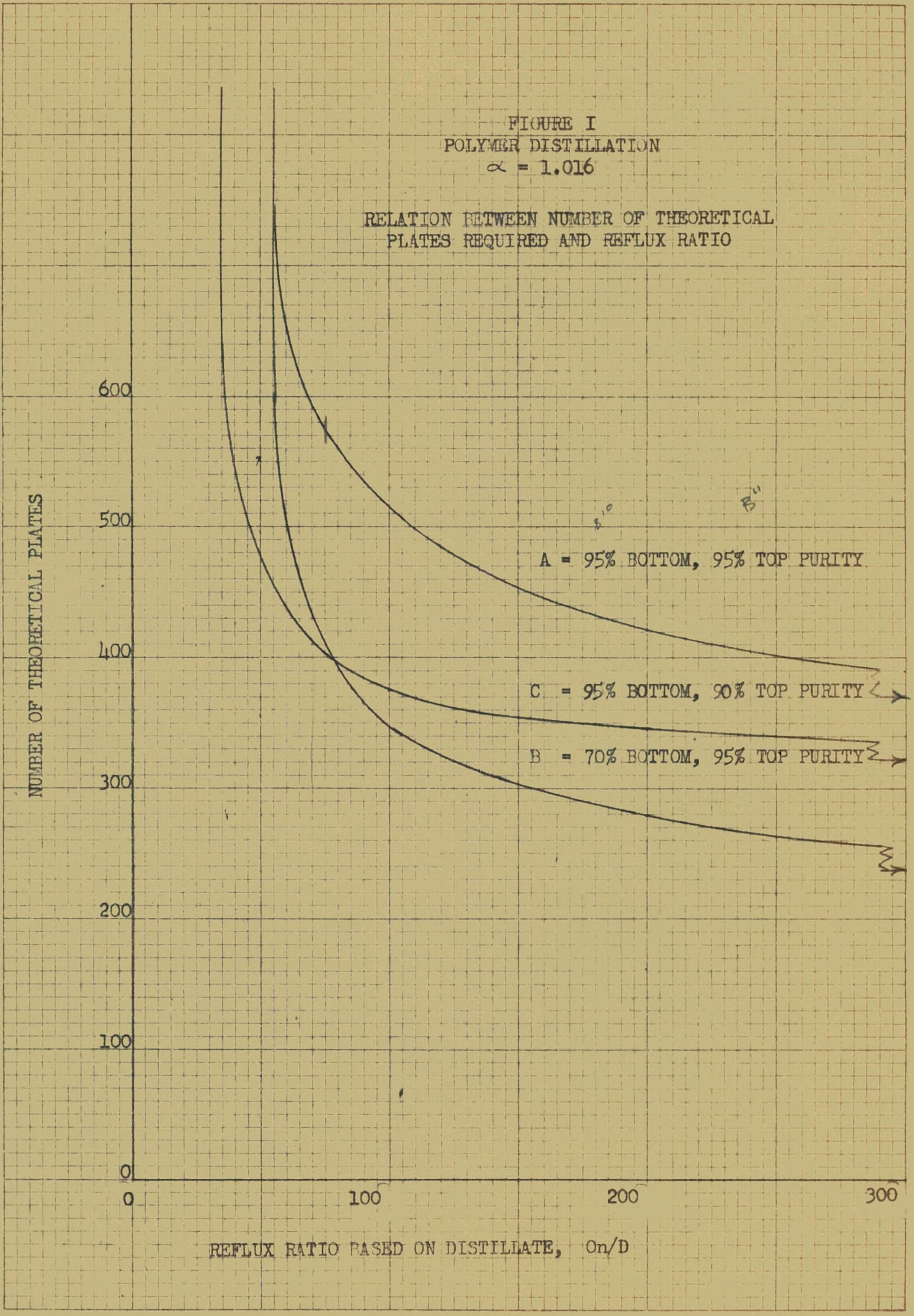

FIGURE I
POLYMER DISTILLATION
$\alpha = 1.016$

RELATION BETWEEN NUMBER OF THEORETICAL PLATES REQUIRED AND REFLUX RATIO

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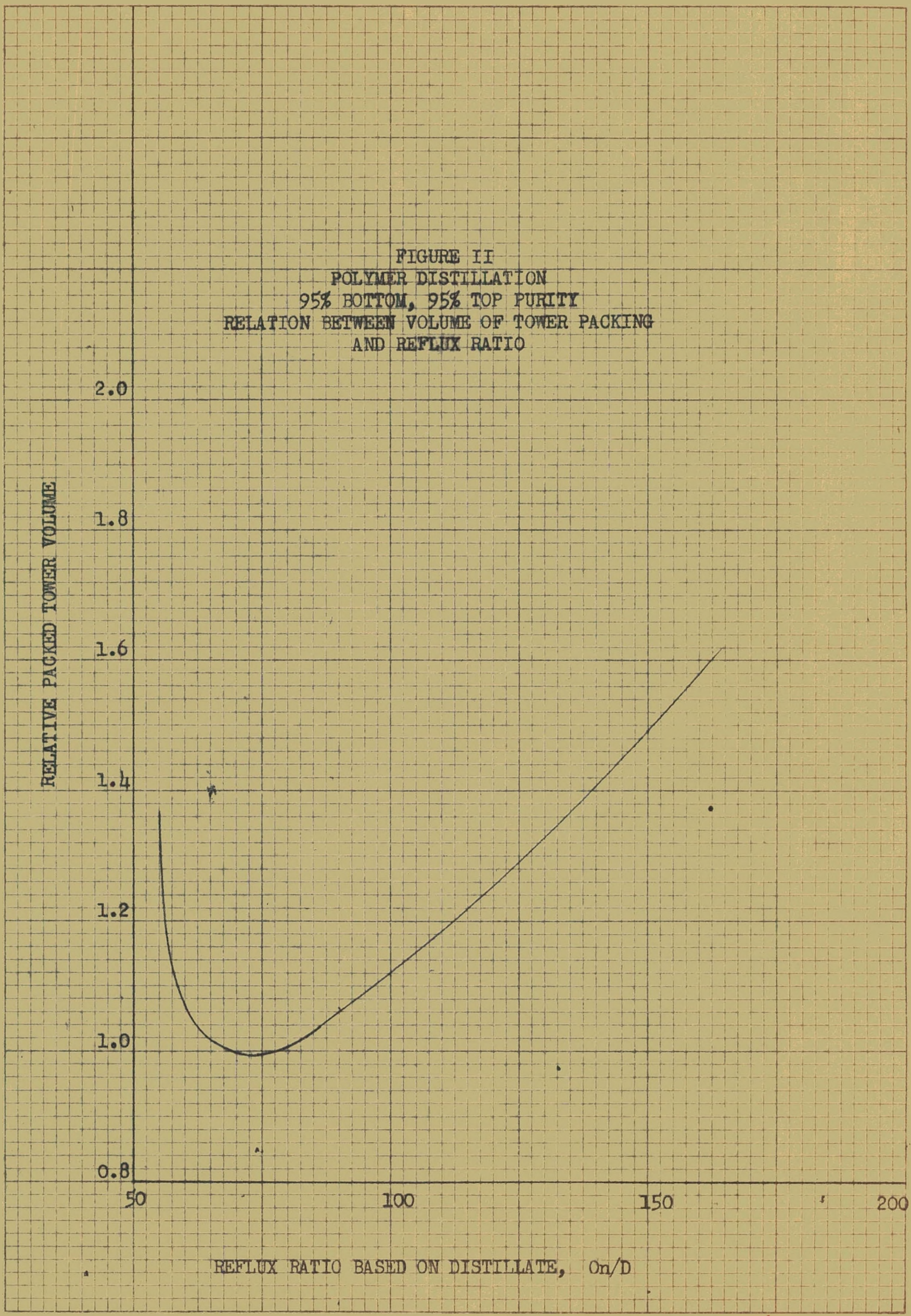

FIGURE II
POLYMER DISTILLATION
95% BOTTOM, 95% TOP PURITY
RELATION BETWEEN VOLUME OF TOWER PACKING
AND REFLUX RATIO

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theoretical plates. This is approximately equivalent to increasing the recovery of the desired isotope in the feed from 50% to 75%. Since this recovery seemed readily obtainable, a 95% overhead purity was chosen as the basis for design.

For the present design a reflux ratio of 80 to 1 based on the overhead product was chosen. This necessitates 561 theoretical plates for a separation giving an overhead purity of 95% and bottom purity of 95%. This reflux ratio results in a tower volume which is near the minimum for the separation as shown in Figure II. Since the amount of decomposition of the polymer is related directly to the tower volume, it is desirable to keep the tower volume at a minimum.

d. Special Process Design Considerations

In the calculations of the number of theoretical plates required for the separation, the usual assumption of adiabatic operation was made. However, the heat loss from the reboiler to the condenser in the system is not negligible in this case. Using blowers between the columns results in some heat input which more than counteracts the radiation heat loss from the system. Under actual operating conditions in the case where a 95% concentration is obtained in the top and bottom product, the liquid reflux decreases about 40 percent from the top to the reboiler if no intermediate cooling is provided. This would result in considerable curvature of the operating line used in calculating the number of theoretical plates and increase the number of plates required. However, by introducing some cooling between columns it is possible to obtain a constant reflux rate to all the columns. It is planned to put small double pipe coolers on the reflux lines to all columnsexcept the first for control of this effect. The reflux to the first column will be passed through a heater so that it can be returned from the overhead accumulator at its boiling point.

Using methyl fluoride recycle in the distillation column, some overhead product will be carried by the recycle to the column reboiler. This, of course, defeats the purpose of the separation and must be reduced to a negligible effect. For a separation of 95% top and bottom concentration it was found that a concentration of .005 mol % polymer in the recycle increased the number of theoretical plates from 561 to 576. For design purposes an allowable concentration of .001 mol % was taken as having negligible effect. This value can be readily obtained either with a solid adsorbent or a liquid scrubbing medium. Depending upon the choice of solvent and liquid volume, approximately eight theoretical plates are required in the scrubber so the liquid scrubbing system appears to be the simplest choice.

e. Use of Old Equipment

We have been advised that the three 18" and the three 12" monel Stedman packed columns used during the previous plant operations, together with their reboilers, condensers, and pumps, can be made available for the present project. (The availability of the 6" columns is uncertain, and they have not been considered here, because of that and because of their small size).

A plant design has been prepared, (Case VI of the cost estimates) based on the use of new columns to rectify the feed and strip it to a concentration at which the balance of the stripping could be effected in the three old 18" and the three old 12" columns. For a production of 750 kilograms per year of boron 10 at a 95% concentration, operating at a column base pressure of 300 mm. mercury absolute, it was found that three 12" columns with 209 theoretical plates would concentrate polymer from 83% to 95%, operating at a bottoms reflux ratio of 65.6. The three 18" columns would concentrate polymer from 41.4% to 83%, operating at a bottoms reflux ratio of 140.9.

To enrich feed from 18.8% to 41.4% at a bottoms reflux ratio of 448 (the same as used in Case V which utilizes 43 foot new columns) will require new columns having 78 theoretical plates, while the rectifying section, operating with an overhead reflux ratio of 80 (also the same as Case V) will require new columns having 176 theoretical plates. Thus the new columns required will be approximately half (45%) of the total required in Case V. The estimate for Case VI has been based on supplying half as many (10) new columns as are used in Case V.

Since the old columns are approximately forty feet high, it was considered advisable to supply new columns of approximately that same height rather than the taller columns used in Case I.

The disadvantages of using the old columns must be evaluated in determining the advisability of using them. These disadvantages are :

(1.) The expenses involved in shipping, testing, inspecting and reconditioning used equipment. These columns are constructed of short flanged sections. These flanges will require cleaning, and in some cases may require refacing. The Stedman packing requires precise fitting in the columns. Considerable work may be required to check the condition of the fit of the packing and correct it if it is found incorrect.

(2) The present laboratory program indicates that recirculation of methyl fluoride with operation at atmospheric pressure will minimize thermal degradation of the polymer and avoid the necessity for operation under vacuum. Operation in this manner would be more complicated with a system containing three sizes of columns, than with one containing columns of one size, since in the former case, recycle methyl fluoride must be introduced at three different points, with three flow rates to be controlled, as compared with one entry point and one recycle gas flow rate in the latter case. It would also be necessary to replace the present condensers on the old columns with blowers, or to supplement them with blowers.

(3) Operation of a fractionation plant containing three sizes of columns will be more complicated than that containing only columns of one size, since in the former case, three sets of reboilers, blowers (or condensers), and reflux pumps must be regulated, due to the three reflux ratios employed, while in the latter case only one reflux flow and one recycle gas rate are flow controlled, and all other flow quantities are controlled by level control or pressure control.

An alternate method of utilizing the old columns would be to set them up as a separate unit, operate them as they were operated before, and obtain additional production in a second unit. The relatively small cost difference between Cases I and III of the cost estimates indicates that such a course would be undesirable, both from the investment standpoint and from the standpoint of operating expense, since more operators would be required for two separate units than for one of larger capacity.

f. Final Design

(1.) Process Specifications

(a) Dissociation of ether-boron trifluoride complex as vapor in columns, 61%.

(b) Blower suction pressure, 14.7 psia

(c) All new columns to be packed with 1 inch Intalox packing.

(d) The HETP for 1 inch Intalox has been taken as 14 inches.

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(e) Vapor velocity; flooding 7.42 ft/sec., design at 60% of flooding maximum.

(f) Reflux ratio based upon overhead product, 80

(g) Polymer partial pressure at base of tower, 300 mm of Hg., temperature 222°F.

(h) Recycle methyl fluoride, 69% by volume of total vapor leaving reboiler.

(i) Liquid holdup in packing .0439 ft^3/ft^3 of packing.

(j) Pressure drop in packing 1.0 inch H_2O/foot of packing.

(k) Blowers sized for 85% of flooding.

(l) Reflux ratio based upon overhead product, 80.

(m) Capacity of old equipment from Standard of Indiana is based upon operating data and 70% of flooding.

(n) A 90% onstream factor is used.

(2.) Cases Evaluated

A number of variations have been considered in the design of the isotope fractionation sections. These along with the different capacities and purities desired result in the following cases:

I Capacity 750 kilograms per year of light boron isotope; isotopic concentration of light polymer and light boron product, 95%; concentration of heavy polymer by-product, 95%; eight tower sections with 82 feet of packing each.

II Capacity 750 kilograms per year of light boron isotope; isotopic concentration light polymer and light boron product, 70%; concentration of heavy polymer by-product, 95%; five tower sections with 86 feet of packing each.

III Same as I except capacity reduced to 500 kilograms per year of light isotope.

IV Same as II except capacity reduced to 500 kilograms per year of light isotope.

V Same as I except that twenty tower sections with only 33 feet of packing each are used.

VI Same as V except three eighteen-inch columns and three twelve-inch available from the plant equipment at Standard of Indiana along with ten new columns with 33 feet of packing are used.

(3.) Process Description

The flowsheet shown in Drawing F4111-1 is based on Case I, but the other cases differ only in the number of tower sections. As indicated, a large number of plates are required for the desired separation. In order to obtain the necessary total height of packing, column sections operating in series as a single fractionating unit having an enriching and stripping section are used. The liquid flow is fed into the top of the first column as reflux and is picked up at the bottom of this column section by a pump and fed into the top of the next column. This is repeated until the bottom of the last column which is equipped with the reboiler is reached. The vapor flow is in the opposite direction. Starting at the reboiler the vapor leaves the top of the last column and is fed into the bottom of the next to the last column. This is repeated until the vapor leaves the top of the first column and enters the condenser and liquid accumulator system. Blowers are provided for the overhead vapor on each column to overcome the cumulative pressure drop through the system.

Recycle methyl fluoride enters at the reboiler and passes through the column with the vapor. At the condenser the polymer is condensed and passing to the accumulator is collected and separated from the methyl fluoride. The methyl fluoride containing a small amount (less than 1.0% polymer) leaves the accumulator and is scrubbed with a suitable solvent for essentially complete removal of the polymer before being returned to the distillation column reboiler. The solvent is stripped of polymer in a reboiler stripper. Purified methyl fluoride is used as a stripping gas using a blower to boost the pressure on a small side stream of the main methyl fluoride stream. The overhead gas from the stripper is returned to the distillation column condenser where it is joined by the distillation overhead vapor.

The feed to the fractionation column is introduced at the suction side of reflux pump P-2 located at the bottom of the second column C-2. The location of the feed point is not too critical in this separation although for the most efficient pperation it should be relatively close to the calculated feed plate. In the cases under consideration feeding at a point between two of the columns is satisfactory.

The fractionation products are withdrawn from the system as liquids. The bottom product is taken from the reboiler. Since there is a possibility of an accumulation of solids in the reboiler, the reboiler liquid is circulated by pump P-11 through a small centrifuge to maintain the solid contamination of the liquid in the reboiler at a minimum. The overhead product is taken at the outlet of the first liquid reflux pump, P-1.

Various blowers for boosting the pressures of the vapor between columns were investigated. The most suitable appears to be the Roots Connersville Type RCG special gas pump. This unit equipped with mechanical seals should be virtually leak proof and give little or no operating difficulty. The unit is a rotary type and can handle appreciable amounts of liquid along with the gas. In order to avoid excessive temperature rise a small stream of liquid may be injected into the blower inlet. The liquid can most conveniently be taken from the pump on the column into which the blower is discharging.

For continuous operation of the fractionation unit it is desirable to have spares on all the mechanical equipment which are essential to the operation. All pumps have been provided with spares. The blowers have been provided with common spares, one spare to two active blowers. Actually the blowers could be used without spares since the fractionation columns could operate with one or two blowers not functioning. However, to minimize the effect on the system if a blower needs repairs, spare blowers are provided.

Steam is required in this section for the operation of the fractionation column. A small steam generator is included in the plant but is not shown on the flowsheet or layout since it will be located outside the immediate distillation area. At the Middlesex location a separate boiler building is available and could be used to house the steam generator.

Control of the unit is quite important in order to maintain the best separation possible. Control instruments are used at all points necessary to make the unit completely automatic. The instrument controlled variables are recorded as are some other variables necessary for analyzing the day to day operation.

The reflux rate is regulated to the first column by an orifice actuated flow controller. The amount of liquid to the following column is determined by the total liquid reaching the bottom of the previous column. A liquid level controller actuating a motor valve on the reflux pump outlet prevents vapor from entering the pump suction. Rotameters are provided in all the liquid lines to aid in the startup operation and in maintaining uniform liquid flow to all columns.

The vapor flow is initially set by the boil-up in the fractionator reboiler. This is controlled by the liquid level in the reboiler which regulates the steam rate to the reboiler coil. The transfer of vapor by the blower is controlled by the suction pressure to the blower which is used through a suitable transducer and transmitter to actuate a motor valve by-passing the blower.

The rate of polymer feed to the distillation zone is controlled by a metering pump since the flow is relatively small. The rate of product removal from the reboiler is set by a hand control valve and measured by a rotameter. The rate of removal of overhead is controlled by the liquid level in the overhead accumulator. Since all these streams are very small compared to the vapor and liquid circulating in the column and the holdup in the system is relatively large, the control of these streams is not critical.

The recycle methyl fluoride is controlled by an orifice actuated flow controller. A similar type of flow controller is used on the scrubbing solvent to the methyl fluoride purification tower. A liquid level controller on the bottom of the absorption tower is used to maintain a liquid seal as the pump suction. The methyl fluoride for stripping is controlled by an orifice actuated rate of flow controller regulating the by-pass motor valve on the blower.

Other instrumentation is provided to aid in startup and detection of operating difficulties. Differential pressure recorders are shown across each column. Thermocouples are placed at a number of points and some of the more important temperatures such as reboiler, blower suction and discharge, condenser and reflux liquid lines are recorded. All the thermocouples are read on an electronic temperature indicator equipped with switches for picking the desired thermocouple leads.

A tentative plant layout is shown in Drawing E 4111-1. This is also based on Case I and the use of the building at the Middlesex location. The columns are arranged on a nearly square pattern with three sections on a side. The purpose of this arrangement is to minimize the wind loading on the column structure, which extends considerably above the intended building. The column structure is completely self-supporting and totally enclosed for security purposes. The associated equipment is located in the area around the base of the columns. All critical equipment is on ground level.

(4.) Material Balances and Process Requirements

The material balances were prepared for the six cases using an arbitrary rate of decomposition of approximately 10 per cent of the feed per day for the cases involving the high purity product and approximately 7 per cent for the cases involving the low purity product. These are shown in Tables B through E. Table B represents Cases I, V, and VI since these have identical material balances.

The process requirements are given in Table F.

TABLE B

Material Balance

Cases I, V and VI

Nominal Capacity 750 kg/yr light boron, 95% purity
lbs. per stream day

	(1) Feed	(2) Feed	(3) Column Feed	(4) Column Overhead Vapor	(5) Column Top Reflux
BF_3	315.4				
$(CH_3)_2O$		214.4			
CH_3F				38,907.7	
$(H_3CO)_3B.2BF_3$				3,105.6	3,068.6
Light $(CH_3)_2O.BF_3$			98.9	1,653.7	1,634.0
Heavy $(CH_3)_2O.BF_3$			430.9	31,601.9	31,225.4
Solvent					
Total	315.4	214.4	529.8	75,268.9	35,928.0

	(6) Condenser Off-Gas	(7) Gas Recycle	(8) Stripper Gas	(9) Stripper Off-Gas	(10) Rich Solvent
BF_3					
$(CH_3)_2O$					
CH_3F	46,694.5	38,891.8	7,786.8	7,786.8	
$(H_3CO)_3B.2BF_3$	115.2			115.2	115.2
Light $(CH_3)_2O.BF_3$	61.2			61.2	61.2
Heavy $(CH_3)_2O.BF_3$	1,172.5			1,172.5	1,172.5
Solvent					15,607.1
Total	48,043.4	38,891.8	7,786.8	9,135.7	16,956.02

	(11) Lean Solvent	(12) By-Product	(13) Product	(14) By-Product
BF_3				
$(CH_3)_2O$				
CH_3F				15.9
$(H_3CO)_3B.2BF$		37.0		
Light $(CH_3)_2\ O.BF_3$		19.7	76.6	
Heavy $(CH_3)_2\ O.BF_3$		376.5	4.1	
Solvent	15,607.1			
Total	15,607.1	433.2	80.7	15.9

TABLE C

Material Balance

Case II

Nominal Capacity 750 kg/yr light boron, 70% purity
lbs. per stream day

	(1) Feed	(2) Feed	(3) Column Feed	(4) Column Over-Head Vapor	(5) Column Top Reflux
BF_3	309.4				
$(CH_3)_2O$		210.3			
CH_3F				38,907.7	
$(H_3CO)_3B.2BF_3$				2,036.0	2,011.5
Light $(CH_3)_2O.BF_3$			97.1	1,545.8	1,527.2
Heavy $(CH_3)_2O.BF_3$			422.6	29,609.6	29,253.3
Solvent					
Total	309.4	210.3	519.7	72,099.1	32,792.0

	(6) Condenser Off-Gas	(7) Gas Recycle	(8) Stripper Gas	(9) Stripper Off-Gas	(10) Rich Solvent
BF_3					
$(CH_3)_2O$					
CH_3F	46694.5	38897.2	7786.8	7786.8	
$(H_3CO)_3B.2BF_3$	80.6			80.6	80.6
Light $(CH_3)_2O.$ BF_3	61.2			61.2	61.2
Heavy $(CH_3)_2).$ BF_3	1172.5			1172.5	1172.5
Solvent					15607.1
	48008.8	38897.2	7786.8	9101.1	16921.4

	(11) Lean Solvent	(12) Byproduct	(13) Product	(14) Byproduct
BF_3				
$(CH_3)_2O$				
CH_3F				10.5
$(H_3CO)_3B.2BF_3$		24.5		
Light $(CH_3)_2O.BF_3$		18.6	76.7	
Heavy $(CH_3)_2O.BF_3$		356.3	33.1	
Solvent	15607.1			
	15607.1	399.4	109.8	10.5

TABLE D

Material Balance

Case III

Nominal Capacity - 500 kg/yr. of light boron, 95% purity
lbs. per stream day

	(1) Feed	(2) Feed	(3) Column Feed	(4) Column Overhead Vapor	(5) Column Top Reflux
BF_3	210.3				
$(CH_3)_2O$		142.9			
CH_3F			0.1866 wt fr. B.	25,938.5	
$(H_3CO)_3B.2BF_3$				2,070.4	2,045.7
Light $(CH_3)_2O.BF_3$			65.9	1,102.4	1,089.3
Heavy $(CH_3)_2O.BF_3$			287.3	21,068.0	20,817.0
Solvent					
Total	210.3 +	142.9 →	353.2	50,179.3	23,952.0

	(6) Condenser Off-Gas	(7) Gas Recycle	(8) Stripping Gas	(9) Stripper Off-Gas	(10) Rich Solvent
BF_3					
$(CH_3)_2O$					
CH_3F	31,129.7	25,927.9	5,191.2	5,191.2	
$(H_3CO)_3B.2BF_3$	76.8			76.8	76.8
Light $(CH_3)_2O.BF_3$	40.8			40.8	40.8
Heavy $(CH_3)_2O.BF_3$	781.7			781.7	781.7
Solvent					10,404.7
Total	32,029.0	25,927.9	5,191.2	6,090.5	11,304.0

	(11) Lean Solvent	(12) By-Product	(13) Product	(14) By-Product
BF_3				
$(CH_3)_2O$				
CH_3F				10.6
$(H_3CO)_3B.2BF$		24.7		
Light $(CH_3)_2$ $O.BF_3$		13.1	51.1	
Heavy $(CH_3)_2$ $O.BF_3$		251.0	2.7	
Solvent	10,404.7			
Total	10,404.7	288.8	53.8	10.6

TABLE E

Material Balance

Case IV

Nominal Capacity 500 kg/yr light boron, 70% purity
lbs. per stream day

	(1) Feed	(2) Feed	(3) Column Feed	(4) Column Over-Head Vapor	(5) Column Top Reflux
BF_3	206.3				
$(CH_3)_2O$		140.2			
CH_3F				25,938.5	
$(H_3CO)_3B.2BF_3$				1,357.5	1,341.2
Light $(CH_3)_2O.BF_3$			64.7	1,030.6	1,018.2
Heavy $(CH_3)_2O.BF_3$			281.8	19,742.2	19,504.6
Solvent					
Total	206.3	140.2	346.5	48,068.8	21,864.0

	(6) Condenser Off-Gas	(7) Gas Recycle	(8) Stripper Gas	(9) Stripper Off-Gas	(10) Rich Solvent
BF_3					
$(CH_3)_2O$					
CH_3F	31,129.7	25,931.5	5,191.2	5,191.2	
$(H_3CO)_3B.2BF$	53.7			53.7	53.7
Light $(CH_3)_2O.BF_3$	40.8			40.8	40.8
Heavy $(CH_3)_2O.BF_3$	781.7			781.7	781.7
Solvent					10,404.7
	32,005.9	25,931.5	5,191.2	6,067.4	11,280.9

	(11) Lean Solvent	(12) By Product	(13) Product	(14) By Product
BF_3				
$(CH_3)_2O$				
CH_3F				7.0
$(H_3CO)_3$ B.2BF		16.3		
Light $(CH_3)_2O.BF_3$		12.4	51.1	
Heavy $(CH_3)_2).BF_3$		237.6	22.1	
Solvent	10,404.7			
	10,404.7	266.3	73.2	7.0

TABLE F

Process Requirements

Isotope Separation Section

Case	I	II	III	IV	V	VI
Power, kw	205	133	143	93	215	117
Cooling Water, gpm	750	750	520	520	750	1,525
Fuel Gas, SCF/Hr.	1,100	1,100	730	730	1,100	2,640
Manpower, total payroll						
Operators	13	13	13	13	13	13
Supervisor(1)	2	2	2	2	2	2
Maintenance(1)	1	1	1	1	1	1
Raw Materials, lbs/day						
Boron trifluoride	315.4	309.4	210.3	206.3	315.4	315.4
Methyl ether	214.4	210.3	142.9	140.2	214.4	214.4

(1) Maintenance and supervisors apply to both sections of plant.

B. Preparation of the Metal from Polymer

1. Preliminary Investigations

The process previously used by American Cyanamid for preparing crystalline boron from the "polymer" ($(CH_3)_2O.BF_3$) produced in the fractionation step was reviewed by a study of the reports submitted by AEC, discussions with AEC representatives, a brief study of literature and patents relating to the art and a discussion on February 25th with personnel of American Cyanamid at Stamford, Conn. Concurrently a study of available alternate processes was started. Since no other method was immediately found which was sufficiently developed and available for use and since the time allowed was short it was decided to base the estimates on the previous operation, and to study the alternate methods discussed below as a secondary consideration.

2. Process Selected

a. Design Considerations

The process as carried out by American Cyanamid consisted principally of four main steps and a number of side-stream recovery steps. The main steps are as follows:

Step 1. $2(CH_3)_2O.BF_3 + CaF_2 \longrightarrow 2\ BF_3.CaF_2 + 2(CH_3)_2O$

Step 2. $2\ BF_3.CaF_2 \longrightarrow CaF_2 + 2\ BF_3$

Step 3. $BF_3 + AlCl_3 \longrightarrow AlF_3 + BCl_3$

Step 4. $2\ BCl_3 + 3H_2 \longrightarrow 6\ HCl + 2B$

More details on these steps and the recovery steps may be found in the American Cyanamid reports.

After a study of the previous operations a few modifications were made in order to simplify the plant and its operations as summarized

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below. Otherwise all the apparatus and processing methods employed are patterned after those used previously. The recommendations of the previous operators for changes in materials of construction have been followed throughout.

(1) Elimination of miscellaneous recovery steps.

The previous operators were forced to employ a number of sidestream recovery operations in order to maintain as high a yield as possible due to the limited quantity of polymer available. It was felt that the elimination of these steps would save enough in apparatus and operating labor costs to pay for the additional polymer production capacity required and result in a much simpler plant to operate. Steps eliminated by this action include "tar recovery", "attachments recovery" (sink and float), "K salt recovery" and "wire recovery". In all, the overall yield of polymer to product was reduced from 82.5% to approximately 74%.

(2) Consolidation of Equipment for Steps 1 and 2

In the previous operations the solid complex ($2BF_3 \cdot CaF_2$) left after removing the monomer in Step 1 was removed from the dough mixer and placed into a gas heated kettle for performing Step 2. The only apparent reason for this was that the dough mixer used could not be heated to a high enough temperature for Step 2. In order to reduce the equipment required and to eliminate a potentially hazardous material handling step it is planned to provide agitated kettles suitable for carrying out Steps 1 and 2 consecutively in the same apparatus. The use of a Dowtherm heating and cooling system in the jackets of these kettles and suitable internal agitation will provide all the features employed in the previous operations. It should be quite practical to reuse the CaF_2 charge several times without emptying the kettles thus reducing product losses somewhat.

(3) Use of Norton Company Apparatus for Step 4

Due to the production rate planned for this plant, the large number of hot wire reduction tubes required would create a major operating problem if their size and capacity were not increased. Therefore, it was felt desirable to consolidate the entire reduction equipment requirement into a single unit with only one electrical control circuit and one process piping setup. Such an apparatus was designed and operated by Norton Company for producing crystalline boron for the U.S. Engineers Manhattan District during World War II. This is described fully in U.S. Patent 2,542,916. A brief description is given elsewhere in this report along with a diagram of the apparatus obtained from the patent. The fact that this apparatus operated successfully is confirmed in National Nuclear Energy Series, Division III, Volume 5 where the operation and the result are summarized. Since the hot elements employed in the apparatus are graphite rods, the principal impurity in the final product would be carbon. Although the product specifications do not specifically limit the carbon content and it has been demonstrated that the specifications for overall purity can be obtained in this apparatus, it would probably be desirable to clear this matter with the ultimate consumer of the crystalline boron. In the event that carbon cannot be tolerated, the possibility of employing boron or tantalum sleeves for the carbon rods should be explored. The use of the Norton apparatus would have an additional advantage over the previously used method in that the high cost of tantalum-tungsten wire would be eliminated. This alone contributed over $90 per pound to the cost of the boron produced. The alternate schemes have been compared further below.

b. Description of Process and Apparatus

The flowsheet for the preparation of crystalline boron from polymer prepared in the fractionation plant is shown on Drawing F-4111-2. A suggested equipment layout is shown in drawing E-4111-2. The designation of the vessels and heat exchange equipment is given in Table G . In the design presented in the flowsheet, the polymer from the fractionation plant is pumped to the polymer storage tank which is located on the second floor. This tank has the capacity to hold one week's production from the fractionation plant and is equipped with a nitrogen blanketing system to prevent the polymer from coming in contact with the moisture in the air. The reagent grade CaF_2 is also stored in the second floor. Before using, the CaF_2 is weighed and then dried in a small electric oven to remove the last traces of moisture. When a reaction kettle is ready to be charged, the CaF_2 is taken from the electric oven while it is still hot and poured by hand into a chute through which it flows by gravity into the reaction kettle. The small polymer metering tank is filled by gravity from the polymer storage tank. This tank has the capacity to hold the polymer for one batch run.

During Step 1 in the preparation of boron, the polymer is added to the reaction kettle in such a way that the boil-off of $(CH_3)_2O$ from the kettle is steady but not rapid. In Step 1 the rate of the reaction is controlled by the temperature of the Dowtherm in the jacket of the reaction kettle. This control is manual in so far as the Dowtherm temperature must

TABLE G

Designation of Vessels and Heat Exchange Equipment

Designation	Name of Apparatus	Material of Construction	Special Features
V-101	Polymer Storage Tank	Monel	Nitrogen Blanketed
V-102	Polymer Metering Tank	Monel	
V-103	Reaction Kettle	Inconel Clad	Jacketed for Dowtherm, Agitated
V-104	Reaction Kettle	Inconel Clad	Jacketed for Dowtherm, Agitated
V-105	$(CH_3)_2O$ Dust Filter	Monel	Filled with S.S. Wool
V-106	Polymer Receiver	Monel	
V-107	Monomer Scale Tank	Monel	Jacketed for Refrigeration
V-108	BF_3 Dust Filter	Inconel	Jacketed for Dowtherm
V-109	$AlCl_3$ Columns	Stainless Steel	Jacketed for Dowtherm
V-110	" "	" "	" " "
V-111	" "	" "	" " "
V-112	$AlCl_3$ Dust Traps	" "	Jacketed for Water Cooling
V-113	" " "	" "	" " " "
V-114	" " "	" "	" " " "
V-115	BCl_3 Receiver	" "	Jacketed for Refrigeration
V-116	Crude BCl_3 Storage Tank	" "	Equipped with Cooling Coils
V-117	Purified BCl_3 " "	" "	" " " "
V-118	BCl_3 Distillation Column	" "	
V-119	Hydrogen Purifier	" "	Filled with Copper Catalyst
V-120	Lectrodryer	" "	
V-121	Lectrodryer	" "	
V-122	Norton Reduction Apparatus	" "	
V-123	BCl_3 Condensate Receiver	Copper	
E-101	Polymer Condenser	Monel	
E-102	Monomer Condenser	Monel	Refrigerated to -100°F
E-103	BF_3 Cooler & Tar Condenser	Inconel	
E-104	BCl_3 Condenser	Stainless Steel	Refrigerated to 30°F
E-105	" "	" "	" " "
E-106	" "	" "	" " "
E-107	Final BCl_3 Condenser	" "	Refrigerated to -100°F
E-108	Distillation Column Reboiler	" "	
E-109	Distillation Column Condenser	" "	Refrigerated to -100°F
E-110	BCl_3 Vaporizer	" "	Equipped with Electric Inversion heater
E-111	H_2 Heat Exchanger	" "	
E-112	H_2 Cooler	" "	
E-113	Tail Gas Cooler	" "	
E-114	Tail Gas Heat Exchanger	Copper	
E-115	Tail Gas Condenser	"	Cooled by Liquid N_2

be changed manually as the reaction progresses. However, the temperature of the Dowtherm is automatically maintained constant at the temperature chosen. The $(CH_3)_2O$ evolved in Step 1 passes through a dust filter to remove any CaF2 that has been entrained in it. The $(CH_3)_2O$ is then cooled to room temperature in a water cooled condenser where any polymer if present is condensed out and recovered. Finally the $(CH_3)_2O$ is condensed in a condenser refrigerated to -100°F and periodically weighed to follow the progress of the reaction in Step 1. Step 1 is completed by purging the $(CH_3)_2O$ from the reaction kettle with nitrogen. The time schedule for Step 1 is given below:

	Operation	Time Required
1.	Load reaction kettle with CaF_2 (Necessary only once or twice a week)	0.3 hr.
2.	Heat reaction kettle to initial reaction temperature of 130°F. Then start polymer addition	0.5 hr.
3.	Reaction period when $(CH_3)_2O$ is evolved. Temperature is slowly increased as reaction progresses	5.5 hr.
4.	Purge reaction kettle with nitrogen to sweep out $(CH_3)_2O$	1.0 hr.

Steps 2 and 3 are carried out simultaneously with the reaction kettle connected by proper valve setting to the feed line to the $AlCl_3$ columns. The reaction kettle temperature is increased until BF_3 is evolved. As the gas also contains some highboiling "tars" fromed by side reactions with impurities and moisture, it is passed through a dust filter, to remove any solids that may have been entrained, and a water cooled condenser where the tars are condensed and the BF_3 is cooled to room temperature. The dust filter as well as the process piping to it are Dowtherm jacketed to prevent condensation of the "tars". The rate at which BF_2 is evolved in Step 2 is held more or less constant by using the reaction kettle pressure to control the temperature of the Dowtherm in the kettle jacket. Step 2 is completed by purging the BF_3 from the reaction kettle with nitrogen. The time schedule for Step 2 is given below.

	Operation	Time Required
1.	Heat reaction kettle to initial reaction of 480°F	1.0 hr.
2.	Reaction period where BF_3 is evolved. Temperature is increased as reaction progresses to drive reaction to completion	12.0
3.	Purge reaction kettle with nitrogen to sweep out BF_3 and to cool CaF_2 down for next batch run	1.0

The BF_3 evolved in Step 2 is converted to BCl_3 in Step 3. This is accomplished by passing the BF_3 through reaction columns packed with $AlCl_3$. The $AlCl_3$ is stored on the second floor where it may also be ground as required in a small roll mill and screened to the proper size prior to charging the columns from this floor. Each reaction column is Dowtherm jacketed in two individually controlled zones for control of the reaction temperature. Each reaction column has with it an $AlCl_3$ dust trap and a BCl_3 condenser. This group of equipment acts as an independent unit and has sufficient capacity to convert and condense all the BF_3 in a given batch to BCl_3. Two of these units are used in series, the second unit as a guard to the first unit since "breakthroughs" are the rule rather than the exception. On the next run, the column which was previously second is placed first and a third unit is placed in service while the first unit is re-charged. These three units are so manifolded that they can be used in any sequence. Any BCl_3 that does not condense in the condensers refrigerated to 30°F is removed in a final BCl_3 condenser refrigerated to -100°F. After the run is completed, the BCl_3 produced is metered in the receiving tank and then drained into the crude BCl_3 storage tank which has the capacity of a week's production of BCl_3. This storage tank is maintained at 30°F by circulating brine. The time schedule to Step 3 followsthat of Step 2 since the two steps are carried on simultaneously. The column containing the AlF_3 (and unreacted $AlCl_3$) is purged with dry air before it is unloaded. Exhaust ducts are provided at the top and bottom of each $AlCl_3$ column to carry away $AlCl_3$ dust when charging the columns and AlF_3 dust when discharging the columns.

The BCl_3 produced in Step 3 contains a small percentage of impurities such as BF_3, HCl, and etc. These are removed in a continuous Distillation Step. The overhead condenser is maintained at -100°F to minimize the loss of BCl_3. The reboiler is heated with hot water. The purified BCl_3 is collected in a brine cooled storage tank maintained at 30°F. This storage tank for the purified BCl_3 also has sufficient capacity for one week's production of BCl_3 and is nitrogen blanketed. The recycle BCl_3 from Step 4 is also processed in this apparatus.

Up to and including the Distillation Step of this process, the operation is designed for a 3 shift- 7 day week basis. Step 4 is designed for operation on a three shift - 5 day week basis with the final picking, grinding, magnetic separations and packing operations carried out in the daytime only.

In Step 4 the BCl_3 is reduced to crystalline boron. Purified liquid BCl_3 is pumped from the storage tank to the BCl_3 vaporizer. This vaporizer holds sufficient BCl_3 to last for the day. The BCl_3 is vaporized by an electric immersion heater which is controlled by the pressure on the vaporizer. Before metering the BCl_3 in a rotameter, the pressure on the BCl_3 is reduced to give it a slight superheat to prevent any condensation from occurring while flowing through the rotameter. The hydrogen required for the reduction reaction in Step 4 is obtained from a hydrogen trailer unit. To insure purity it is passed over a copper catalyst at 500°F where any oxygen present is converted to water which is subsequently removed in an alumina dryer. The dry hydrogen is then metered through a rotameter and mixed with BCl_3 at the proper ratio. The BCl_3 and hydrogen enter the Norton reduction apparatus near the top, pass over the hot graphite rods, and the H_2 and unreacted BCl_3 flow from the bottom portion of the reaction. The Norton reduction apparatus is shown in Figure III. The apparatus contains six rods (R) connected internally to form three inverted U-shaped assemblies on which the boron is deposited. The internal connections are also graphite, but are of sufficient cross section that they do not reach reaction temperature when the current is flowing. As the thickness of the boron layer increases, the temperature gradient is such that the boron tends to squeeze the carbon rods. Therefore, these rods are of a special slotted construction found necessary to minimize the possibility of fracturing them. If a rod does fracture during operation, the inverted U, of which it is a part, is by-passed electrically and the run is continued at reduced voltage and rate with the remaining rods. The temperature of the rods is measured with an optical

FIGURE III

Feb. 20, 1951 G. H. FETTERLEY **2,542,916**

APPARATUS FOR THE PRODUCTION OF BORON

Filed Aug. 3, 1945 4 Sheets-Sheet 2

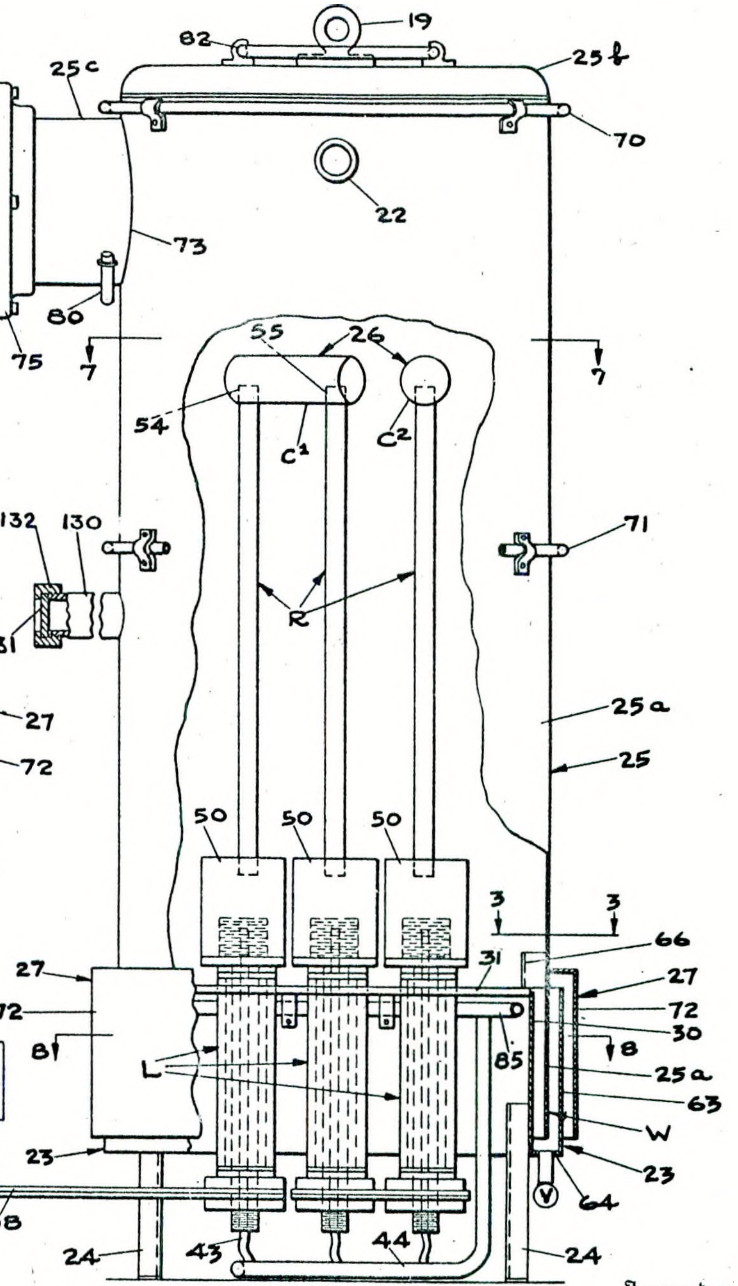
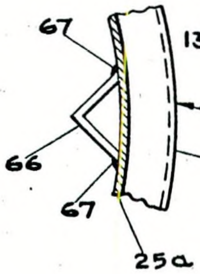


FIG. 2

FIG. 3



Inventor

GUY H. FETTERLEY

By William T Kuesner

Attorney

pyrometer through a sight window 131 and is controlled by varying the voltage on lines 58 and 59 which varies the current flowing through the apparatus. The shell of the apparatus 25 is cooled by a film of water originating at pipe 70 and continuously flowing down the side of the apparatus. The rod mountings L are also water cooled. The apparatus is made gas tight by a high density liquid seal at the bottom. 25a represents the section of the jacket in the liquid seal. A rupture disc is provided at 77. At the end of a run the jacket is raised with a hand hoist and the boron graphite rods are removed and replaced with new graphite rods.

Alternate equipment similar to that used by American Cyanamid for the reduction step is shown on the flowsheet above the Norton apparatus. These units have the same capacity as those previously used but are fabricated from standard glass pipe and are mounted vertically. They contain tantalum-tungsten wires as used before. A comparison of the operating cost for the Norton apparatus with the nine Pyrex glass pipe units required for a plant having a capacity of 750 Kg/Yr at a 95% concentration of boron 10 is given below. It has been estimated that the initial costs would be about the same for both types of apparatus.

Comparison of Operating Costs of Norton Apparatus and Multiple Pyrex Reduction Tubes

Basis: One pound of final product boron of any purity

	Unit Cost	Norton Apparatus	Pyrex Reduction Tubes
Carbon electrodes	$1.50/lb.	$0.97	-----
Tantalum-Tungsten Wire	$116 /lb.	------	$ 89.90
Electric power	0.7¢/Kwh	3.15	1.58
Cooling Water	3.0¢/M gal	0.66	0.33
Operating labor	$2.00/man hr.	9.08	27.24
Savings in operating cost for the Norton apparatus per lb. of Boron		$105.19	

The tail gases from the Norton apparatus (or the reduction tubes) are cooled to room temperature in a water cooled condenser. They are then further cooled in a heat exchange cooled by the final cold tail gases. The BCl_3 and some HCl are condensed in the BCl_3 condenser which is cooled by liquid air. This is returned to the crude BCl_3 storage for recycling. The hydrogen and uncondensed HCl cool the incoming gas and then flow to the tail gas scrubber where these are scrubbed with water to remove the HCl and traces of BCl_3 before the gas is released into the atmosphere. The tail gas streams from Steps 2 and 3 and the Distillation Step are also passed through the water scrubber before being released into the atmosphere.

The refrigeration equipment to serve the various condensing loads is not shown on the flowsheet. However, refrigeration would be provided at 0°F and -100°F temperature levels by a two stage system of Freon 22. Calcium chloride brine is circulated at the higher temperature level, while the refrigerant is expanded directly in the three condensers requiring the low temperature refrigeration.

The graphite rods (or tantalum wires) with the boron deposits are taken into an air conditioned room for the remaining operations to avoid moisture pickup. Here the boron deposit is hand picked from the graphite rods and is then crushed and ground in a ball mill that continuously classifies the material. A photograph and description of a suitable apparatus is given in Figure IV. The boron is continuously fed to the ball mill by a constant weight feeder. The crushed boron is picked up at the exit of the ball mill by an air stream and is carried through a classifier where the coarse material drops out and is recycled to the ball mill. The product boron is then removed from the air stream in a cyclone and the air is recirculated back to the ball mill by a small blower. The product boron is removed from a chute at the bottom of the cyclone after a run is complete. The air circulation system is essentially a closed system. However, a slip stream of the recycled air is passed through a bag filter to remove the extra fine boron that passes through the product cyclone.

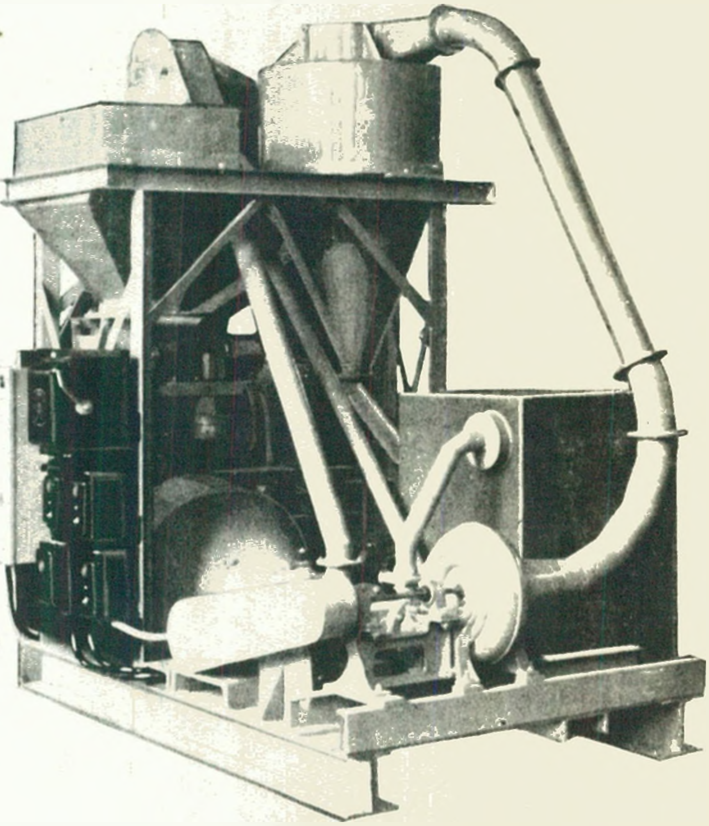
The ground boron product from the ball mill is run through a separate screening operation as a check on the ball mill classifier. The boron of the proper particle size distribution is then passed through a magnetic separator to remove the metallic contaminants picked up in the grinding operation. The boron is then ready for packaging.

c. Material, Utility and Labor Requirements

There are four cases under consideration for the preparation of the metal from polymer. They are defined in the step for the

for DRY GRINDING

FIGURE IV



the HARDINGE *Pilot Plant* *or* *Laboratory Unit* *for* *Dry Grinding*

PORTABLE GRINDING AND CLASSIFYING EQUIPMENT

THE UNIT CONSISTS OF

1 • **Size "A" Hardinge** Constant-Weight Feeder **suspended from 3-cubic-feet feed bin.**
2 • **2′ x 8″ Hardinge** Conical Ball or Pebble Mill **with drive motor.**
3 • **A complete** Air Classifying System **consisting of a** No. 12 Loop Classifier, **cyclone product collector, exhaust fan, and all piping.**
4 • **Bag type dust collector for vent.**
5 • **Hardinge** "Electric Ear" **sound control unit.**
6 • **Complete structural steel base and supporting frame.**
7 • **All equipment completely wired. It is only necessary to connect power line.**
8 • **Dimensions of unit: 7′-7″ long, 5′-2″ wide, and 8′-0″ high.**

see reverse side for WET grinding unit

867-049

For complete details and application data on this unit, or information concerning other Hardinge equipment (Mills, Classifiers, Thickeners, Clarifiers, Ruggles-Coles Dryers, Feeders, ABW Sand Filter, etc.), write our nearest office

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preparation of the polymer as Cases I, II, III and IV. The material balances for these cases are given in Table H; the utility summaries are given in Table I. The labor requirements for the four cases are essentially the same and are summarized below according to working schedule:

3 shift - 7 day week schedule	2 operators/shift
3 shift - 5 day week schedule	1 operator /shift
day shift-5 day week schedule	1 operator /shift
Total number of Operators required	13

If the alternate of the reduction tubes is used, it would be necessary to have 3 operators/shift on the 3 shift-5day week schedule. The total number of operators required for this type operation would be 19.

The above labor requirements include only the actual operator required for the preparation of the metal. Supervisory personnel and others that would be required for the operation of the plant as a whole are not included.

d. Recommendations for Further Study on Process Modifications

The time allowed for this study did not permit a full study of some of the improvements that have been proposed for the process as set forth above. It is recommended that further study of the literature and/or in the laboratory be made of the following items.

(1) The possibility of substituting MgF_2 for CaF_2 in Step 1 should be investigated due to the availability of this material as a by-product of other AEC operations.

TABLE H

Material Balance Summary for Preparation of Metal

Bases:

1. Material rates based on 3 shift - 7 day week operation with a 90% on-stream efficiency.
2. Material rates for Steps 4 through Packaging represent calculated rates on above bases since these operations are actually carried out on a weekly basis

Case	I	II	III	IV
Plant Capacity, Kg/yr. of Pure Light Boron Isotope	750	750	500	500
Purity of Light Boron Isotope, Mol %	95	70	95	70
Step 1.				
(a) $BF_3O(CH_3)_2$, lbs/day	80.72	109.79	53.81	73.19
(b) CaF_2, lbs/day (2)	46.81	63.67	31.21	42.43
(c) $(CH_3)_2O$ Collected, lbs/day	31.50	42.85	21.00	28.55
Step 2.				
(a) Tars, lbs/day	2.07	2.82	1.38	1.88
(b) BF_3 given off, lbs/day	44.70	60.80	29.80	40.51
(c) Purge Nitrogen, SCF/day	2,940	4,000	1,970	2,670
Step 3.				
(a) $AlCl_3$, lbs/day (Special Specs)	106.37	144.68	70.91	96.41
(b) Distilled BCl_3, lbs/day	81.35	110.65	54.23	73.73
Step 4.				
(a) Carbon electrodes, lbs/day (1)	3.4	4.62	2.27	3.08
(b) Hydrogen SCF/day	6249.	8500.	4166.	5664.
(c) Liquid Air, liters/day	118	160	78	107
(d) Boron, lbs/day	5.88	8.00	3.92	5.33
Grinding Separating and Packaging				
(a) Boron, lbs/day	5.29	7.20	3.53	4.80
(b) Pure light boron isotope, lbs/day	5.03	5.03	3.35	3.35
(1) Alternate of Reduction Tubes				
(a) Ta-W wire, lbs/day	4.10	5.57	2.73	3.71

(2) Maximum required if fresh charge needed for each batch run

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TABLE I

Summary of Utilities for Preparation of Metal

Bases: Same as for Material Balance Summary

Case	I	II	III	IV
Plant Capacity, Kg/yr. of Pure Light Boron Isotope	750	750	500	500
Purity of Light Boron Isotope, Mol. %	95	70	95	70
1. Electric Power, Kwh/hr.	400	543	267	362
2. Cooling Water, gpm	140	190	94	127
Alternate of Reduction Tubes				
1. Electric Power, Kwh/hr.	310	423	207	282
2. Cooling Water, gpm	100	140	67	91

(2) The optimum operating conditions of the Norton Company reduction apparatus should be determined by conference with Norton Company personnel. In addition to this some investigations should be made of the feasibility of using boron rods or boron sleeves for the graphite rods in this apparatus in order to improve product purity.

(3) A search should be made for a method of selectively removing hydrogen chloride from the tail gases of the reduction apparatus (Step 4) and recycling the unreacted BCl_3 and hydrogen. This would have the triple advantage of

(a) Eliminating liquid air refrigeration requirements.

(b) Eliminating BCl_3 losses in tail gases.

(c) Eliminating the loss of approximately 80% of the purchased hydrogen.

The only process thus far proposed for this consists of passing the tail gases over zinc dust at 200°C at which temoerature, according to one reference, BCl_3 will not react. Aluminum and cadmium have also been suggested as alternates for zinc. If the anhydrous HCl will react with the zinc dust under these conditions sufficiently to remove a quantity each pass equal to that generated it would not be necessary to effect complete removal percentagewise from the gas stream to make the operation feasible.

If it proves impractical to separate the HCl selectively from the tail gases, a study should be made of the feasibility of removing the HCl from the gases after condensing the BCl_3 and recycling the hydrogen. Whether this is economical or not would depend on the cost of obtaining hydrogen and the length of time the plant is to operate. Technical feasibility will depend on whether other reaction products are present in the tail gases which cannot be readily removed and which would have an adverse effect on the reduction.

3. Alternate Processes Considered

a. Processes Investigated

The following paragraphs describe briefly the investigations made of alternate processes for producing the crystalline material from the polymer. Some of these investigations were not complete at the time of writing this report and are so indicated. Recommendations for further work are made separately below.

(1) U. S. Patent 2,415,946 (Issued to W. C. Goss)

At the start of this project AEC personnel suggested that Girdler investigate this patent to determine if the reduction process covered by it could be employed instead of the hot wire process previously employed. Mr. Goss was located, after some difficulty, in Kirkland, Washington and a discussion was held by telephone concerning the status of his process. He stated that the furnace he contemplated using was developed for use in producing activated carbon while working on a Chemical Warfare Service contract. He thought that it might be applicable to boron and tried it on a laboratory scale where he claimed it was successful. One of the advantages claimed for the process was that the product tended to increase in purity as time went on, the initial batch probably being high in boron carbide. The operation would have to be continuous, he claimed, and was best suited to operations up in the tonnage rate of production. Mr. Goss said that he would not be interested in working with Girdler on developing it further unless large quantities of boron were being considered. Since the product from this process is amorphous which would have to be converted to crystalline anyway, it was decided to drop any further consideration of this process.

(2) Production via Diborane

Early in this project AEC personnel suggested the process of producing B_2H_6 from the polymer by reaction with lithium hydride followed by the cracking of B_2H_6 to elemental boron and hydrogen. A visit was made by AEC and Girdler personnel to Argonne National Laboratory to confer with J. J. Katz, the originator of the suggestion. It was learned at this meeting, and at a subsequent meeting of AEC and General Electric personnel at Schenectady, N. Y., that the process for producing B_2H_6 from the diethyl ether complex had been well worked out and was being operated on a small commercial scale. At the present writing it is not known if the subsequent cracking operation has even been carried out in anything but a small laboratory scale. It is also not known if it would be practical to carry out the first part of this reaction with the dimethyl etherate or if it would be necessary to convert it to the diethyl etherate first. Due to these unknown factors it was not possible to make a comparison of the economics of this process with the process previously used. Further investigation should be made of laboratories working on boron chemistry to determine whether the cracking step has ever been performed on a larger scale and if the yields are favorable. Unless this has already been demonstrated it is doubtful whether it should be considered further as the time schedule for completing the production unit would not allow time for an extended development program. (References to this process may be found in AEC memos of A. N. Rogers to Files dated March 2, 1953 and A. N. Rogers and M. C.Kells to Files dated March 6, 1953, a Girdler memo of N. C. Updegraff to R. M. Reed dated February 28, and Report No. 55251, General Electric Company, Schenectady, (designated NP 403) all of which are in AEC NYO files).

(3) Miscellaneous Commercial Production Methods

A list of commercial suppliers of boron obtained from various directories was compiled and telephone contacts made by AEC personnel to determine what reduction processes were employed in industry and what product purities they were able to attain. Three companies were found that produced the material in this country and one additional one that is experimenting on a laboratory scale. The results of this preliminary investigation may be summarized as follows:

1 - F. W. Berk and Company, Woodridge, N.J., produces an 85% purity amorphous material and has produced up to 92% purity in the laboratory. The principal impurity is sodium, apparently from a sodium reduction process.

2 - Metal Salts Corporation, Hawthorne, N.J. produces 85% purity amorphous material. The principal impurity is magnesium, apparently from a magnesium reduction process.

3 - Var-Lac-Oid Chemical Company, New York, is not now a producer but has been doing some laboratory work on the production of a crystalline material.

4 - Cooper Metallurgical Associates, Cleveland, was stated to be the only commercial producer of crystalline boron. Their process was investigated further as described below.

It was decided to eliminate the first three of these companies from consideration at present, and to investigate Cooper Metallurgical Associates process further as described below.

(4) Cooper Metallurgical Associates Process

As a result of an inquiry to this Company it was found that they are employing an electrolytic process in a fused salt bath. They stated that the starting material can be one of several solid boron compounds including oxides and combinations with sodium or potassium. Gaseous compounds have not been used. They claim that they can produce crystalline boron of 99% purity containing 0.28% iron and 0.16% carbon and quote a price of 70¢ per gram in quantities greater than 500 grams.

A brief search in the literature uncovered two patents which apply to this operation, 2,572,248 and 2,572,249. The former discloses that the fused salt bath consists of KBF_4 and KCl. In operation at 650 to 1000°C the following reaction takes place:

$$2\ KBF_4 + 6\ KCl \text{ ----- } 2B + 3Cl_2 + 8KF$$

The chlorine passes off as a gas and the boron deposits on the cathode in what is claimed to be a granular form of crystalline aggregates, which contain water and acid soluble impurities, readily removable from the cathode and purified by washing. In adapting this process to the Polymer Project it should be feasible to react the BF_3 evolved from Step 2 with KF to form the KBF_4 required for this operation. It is possible that this method might be very well suited to the project.

The patent holders are at present unwilling to license them as they would prefer to sell the product themselves. However, it might be possible for AEC to approach this company later if the process appears attractive and make some arrangement with it although it might be necessary to explain the project to them to convince them that the use of their process would neither compete with them or take away a potential market for their product. Under the present security restrictions, Girdler did not feel it advisable to discuss it further with them.

b. Recommendations for Further Study

In view of the above, it is recommended that the following processes be investigated further.

(1) The production of elemental boron from diborane should be investigated further to determine if this has ever been carried out on a pilot plant or commercial scale and if the yields and economics are more attractive than the process selected.

(2) The process employed by Cooper Metallurgical Associates should be investigated further to determine its applicability to the project and whether the owners of the patents can be persuaded to license it. The latter matter would have to be handled by AEC if the process still appears attractive after further investigation.

III. PLANT ESTIMATES

Cost estimates have been prepared for six cases, as follows:

I. Plant for producing 750 kilograms per year of pulverized crystalline boron 10, isotopic concentration 95%, boron concentration greater than 98%, with fractionation of polymer carried out in eight 93 foot columns packed with 1" Intalox saddles.

II. Plant for producing 750 kilograms per year of pulverized crystalline boron 10, isotopic concentration 70%, boron concentration greater than 98%, with fractionation of polymer carried out in five 97 foot columns packed with 1" Intalox saddles.

III. Same as I, except capacity is 500 kilograms per year

IV. Same as II, except capacity is 500 kilograms per year

V. Same as I, except fractionation is carried out in twenty 12 foot columns packed with 1" Intalox saddles.

VI. Same as V, except six Stedman packed columns from the plant operated by Standard of Indiana have been substituted for ten of the twenty columns packed with 1" Intalox saddles.

Estimated costs for the six cases presented in this section include all process equipment requirements and erection labor. Detailed equipment lists were prepared and quotations were obtained on some of the major items. Labor costs were based on rates for the Middlesex, N. J. area. No buildings have been included as it is contemplated using the existing building at Middlesex, However, an estimated cost has been included for removing the existing equipment from this building, decontaminating it and making necessary alterations to adapt it to the Polymer Project. No costs have been included for increasing the power or water service capacity to the site. If it is decided to erect the plant at an alternate site, it would be necessary to review these estimates.

Detailed estimates are described in the following paragraphs. A summary of all the estimates is presented in Table N.

A. Fractionation of Polymer

Table J gives a detailed equipment list for Case I along with specifications for the major equipment. The other cases were estimated by prorating from Case I and detailed equipment lists have not been included. However, the itemized cost estimates for all six cases are given in Table K. In prorating Case I, a number of items had to be considered. These are discussed below:

Case II. Only 70 percent product concentration is required resulting in a reduction in the number of columns from eight to five. In order to have the required number of theoretical plates in five columns the depth of packing is increased to 86 ft. A direct reduction in the equipment associated with the columns is obtained. These include six liquid reflux pumps, four blowers, three liquid level controllers, three rotameters, three back pressure controllers, and other instrumentation.

Case III. The capacity is reduced from 750 kilograms in Case I to 500 kilograms per year. The number of columns required is the same as Case I but the diameter of the columns is reduced from 20 inches to approximately 16 inches. Some reduction in reboiler and condenser area is realized. Similarly some equipment in the recycle purification section is reduced.

Case IV. The capacity is reduced from 750 kilograms in Case II to 500 kilograms per year. This results in the same savings as in Case II with the additional savings shown in Case III for the smaller diameter columns.

Case V. The tall columns in Case I are reduced to shorter ones of the same diameter. Twenty 42 foot columns with 33 feet of packing each are used in place of the eight 93 foot columns. Since the pressure drop is considerably less per column, blowers are needed only every other column. Thus a total of ten active blowers is used. Instrumentation is considerably increased because of the greater number of columns and blowers.

Case VI. Equipment available from the plant operated by Standard Oil of Indiana is used. This equipment includes three 18" and three 12" Stedman packed forty foot columns with reboilers and overhead condensers and the associated liquid pumps for transferring the material between columns. In addition ten 42 foot columns, 20 inches in diameter with five intermediate blowers are necessary to make the plant equivalent to Case V. Nothing has been included in the estimate for the cost of the old equipment from Standard Oil of Indiana or the repair of such equipment. The cost of instrumentation for all the columns has been included, however.

B. Preparation of Metal

Due to the small size of the equipment involved the variations in throughput for the different cases calculated have very little effect on the equipment costs for this portion of the plant. It has been estimated that the total cost spread between the quantities involved in Cases II and III above would be less than 5% for the metal preparation equipment. Therefore, only one detailed estimate is presented in Table L. (Corresponding to Case I above) and the same estimated cost is used for each of the six cases.

C. Utility Section

Cost estimates of certain utility and service facilities which are common to both manufacturing sections of the plant are presented in Table M. Since these vary only slightly between cases the same total cost is used for all of them.

D. Critical Materials

Estimated weights of critical alloys required in the fabrication of the process equipment listed in Tables J and L (Case I) are presented in Table O. All of the equipment items in these lists will require more than 60 day delivery.

TABLE J

Detailed Cost Estimate
Isotope Separation

Case I

NO.	VESSELS ITEM	COST
1	Feed Drier, V-1. Dry gaseous feed stream containing small amount of moisture. Alumina dessicant in fully automatic drying and regenerating unit. Capacity - 12 SCFM, Operating pressure - 25 psig, Operating temperature - 100°F, Material - carbon steel	$ 2,420
1	Liquid - Gas Separator, V-3. 25 gal. volume. Operating temperature - 100°F, Operating pressure - 5 psig, Material - carbon steel, 12" I.D. x 4' w/sight glass	330
1	Feed Storage Tank, V-4. 500 gallon tank. Operating temperature - 100°F, Operating pressure - 5 psig, Material - carbon steel, 4'-0" I.D. x 4'-6"	495
1	Byproduct storage tank, V-4A. 1000 gallon tank. Operating temperature - 100°F, Operating pressure - 5 psig, Material - carbon steel, 4'-0" I.D. x 9'-0".	1,000
1	Overhead Accumulator, V-5. 140 gallon vertical tank. 2' x 6'. Operating temperature - 100°F, Operating pressure - 5 psig, Material - carbon steel	440
8	Distillation Column, C-1 to 8. Vertical packed column, 3 main shell sections, domed cover and base section, liquid distributor plates at the topes of the three sections, packing supports at the bottoms of the three sections, liquid collector rings at the other six foot intervals, 3/16" wall thickness. Diameter - 20" O.D., Main Sections - 24, 24, 36 ft. long, Top Section - 3 ft., Bottom section - 6 ft., total height - 93 ft., Packing 82' of 1" Intalox Saddle,, Operating pressure - 14.7 psia to 18.7 psia, Operating temperature - 222°F., side handholes near top and bottom of each section, connections for liquid and vapor in top section, connection for liquid and vapor, level control, sight glass in bottom section. Material - walls above packing monel, steel flanges, monel internals, steel top section, monel bottom section, steel skirt.	122,400
1	Absorption Column. Purify recycle methyl fluoride. Size 18" I.D. by 25' with 20' of Intalox 1" packing. Operating pressure - 18 psia, temperature 128°F., Material - carbon steel. Includes E-10.	2,200

NO.	ITEM	COST
1	Stripping Column. Recovery of polymer from methyl fluoride scrubbing solvent. Size 10" ID by 25' with 20' of Intalox 1" packing. Operating pressure - 19.7 psig, Temperature - 262°F., Material - carbon steel. Includes E-7.	$1,100
	PUMPS	
16	Reflux Pumps (One active, one spare P-1 through P-8) 4 gpm, 60 psi head, turbine type with mechanical seals, self priming, materials cast iron with brass impeller	7,920
2	Feed Pump (One active, one spare) P-9, Metering pump - 3 gal. per hour, Suction - 0 psig, Discharge - 60 psig, Liquid SG = 1.232 at 25°C Mu = 1.65 at 25°C Materials cast iron with brass impeller	1,100
2	Bottom Product Pump (One active, one spare), P-10 Same as P-1	990
2	Reaction Product Transfer Pump (P-11 one active, one spare) 10 gal. per hour. Suction pressure - 0 psig, Discharge - 20 psig, SG 1.232 at 25°C., Viscosity 1.65 at 25°C. Hills McKanna positive displace. Material iron with brass fittings.	1,540
2	Circulating pumps (1 active, 1 spare) for rich solvent from absorber. P-12. 2 gpm, 20 psig. Material - cast iron and brass impeller	660
2	Circulating pumps (1 active, 1 spare) for lean solvent from stripper. P-13. 2 gpm, 20 psi, Material - cast iron and brass impeller.	660
	BLOWERS	
12	Overhead Vapor Blowers (B-1 - B-8) (One active, plus 1/2 spare) Suction pressure - 14.7 psia, Discharge pressure - 19.7 psia, Gas quantity - 75.7 lbs/min. or 821 ACF/min., Gas temperature (suct.) - 215°F., Gas density (suct.) - .092 lbs/cu. ft. Roots blowers - cast iron - mechanical seals, Type RCG w/30 HP explosion proof motor and starter, V-Belt drive and guard	52,800
2	Stripper gas blowers, 80 SCFM (1 active, 1 spare) B-9, Suction - 17 psia at 100°F., pressure drop - 3 psi., Roots-Connersville 67XA with 5 HP motor and starter. Cast iron - mechanical seals V-belt drive and guard.	3,520

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NO.	ITEM	COST
	HEAT EXCHANGERS	
1	Reaction Cooler and Condenser, E-2. Duty - 44,820 Btu/hr. Surface - 10 sq. ft., Shell Side: Operating temperature - 430°F, Operating pressure - 5 psig, Tube Side: Operating Temperature - 100°F, Operating pressure - 25 psig, Material: Carbon steel shell, carbon steel tubes.	$ 430
1	Overhead Condenser, E-3. Duty - 808,080 Btu/hr., Area - 300 sq.Ft., Shell:- Monel - Operating temperature - 250°F, Operating pressure - 15.7 psig, Tubes: Monel 3/4" O.D., 12 ga., U-bends, annealed after bending, monel spacers and baffles. Tube Sheets: Double construction to prevent water leakage into system, inner sheet monel, carbon steel outer sheet	11,000
1	Reflux Heater, E-4. Duty - 126,000 Btu/Hr., Area - 31 sq. ft. Shell: Carbon steel - Operating temperature 295, Operating pressure 50 psig, Tube: Operating temperature 250°F, Operating pressure 60 psig. Monel Material. Double pipe type exchanger	1,320
1	Reboiler, E-5. Duty: 767,300 Btu/Hr., Area - 384 sq. ft., Shell: Carbon steel - operating temperature 222°F., Operating pressure 15.7 psig, Tubes: Monel, 3/4" O.D., 12 gage, U-bends, annealed after bending. Operating temperature 242°F, Operating pressure 50 psig. Tube Sheets: Carbon steel, double construction to prevent steam leakage into reboiler. Baffles and spacers monel.	12,100
1	Bottom Product Cooler, E-6. Duty: 2240 Btu/hr. max., Area - 2 sq. ft., Shell: Operating temperature 110°F, Operating pressure 25 psig. Tubes: Operating temperature 222°F, Operating pressure 5 psig. Material - Stainless steel	132
1	Stripper overhead cooler. 3.8 sq. ft. in top of stripper column. Copper coil. E-11.	110
1	Solvent heat exchanger - exchange heat between rich and poor solvent. Area 32.3 sq. ft. double pipe type carbon steel. E-8.	660
1	Rich Solvent Heater - heat fluid to stripper. Area 15.4 sq. ft. steam jacketed pipe. Carbon steel. E-9.	440

NO.	ITEM	COST
	INSTRUMENTS	
1	Pressure Controller. Actuate air motor valve to control downstream pressure motor valve. Gas - 325 SCFH, Sp. Gr. = 1.6, 1/2" Body - Needle valve and seat, Upstream pressure - 100 psig. Downstream - 5 psig, Stainless trim, Iron body.	$ 270
1	Pressure Controller. Same as above.	270
8	Pressure Controller Recorder. Actuate motor valve on outlet of blower to control suction pressure. Transmitter. Receiver for panel mounting. Motor valve. Gas - 9000 SCFH sp. gr. = 2.38, 3 in. Butterfly Pressure Drop - 0.1 psig Pressure - 2 psig. Monel trim, steel body.	9,912
8	Differential pressure recorder. Measure pressure differential of vapor across column. Transmitter (Brown Electric Type), Receiver for panel mounting	3,520
8	Reflux Rotameters. (Fischer & Porter). Measure liquid reflux rate to column. Operating capacity - 3.7 gpm, Temperature - 222°F, Pressure - 55 psig, Monel fittings.	1,892
1	Rotameter. Measure gaseous flow MW = 46. Operating Capacity - 326 SCFH, Temperature - 100°F, Pressure - 25 psig, Monel fittings.	160
1	Rotameter. Measure gaseous flow MW = 68. Operating capacity - 326 SCFH, Temperature - 100°F, Pressure - 25 psig, Monel fittings.	160
1	Rotameter. Measure column distillate product on liquid. Operating capacity - 2.2 gpm, 1.12 sp. gr., Temperature - 100°F, Pressure - 10 psig, Monel fittings.	160
1	Rotameter. Measure column bottom product on liquid. Operating capacity - 0.4 gpm 1.12 sp. gr., Temperature - 100°F, Pressure - 10 psig, Monel fittings.	160
1	Liquid Level Controller Recorder. Actuate motor valve controlling liquid by-pass and reaction product pump. Transmitter (Fisher Leveltrol) Receiver for panel mounting (Foxboro) Motor valve. Liquid - 20 gpm sp. gr. 1.12 1/2 in body, needle stem and seat, Pressure 25 psig, Temperature - 100°F, Monel trim, steel body, Float - Stainless steel, Inconel torque tube.	700

NO.	ITEM	COST
1	Liquid Level Controller Recorder. Actuate motor valve controlling distillate product take-off. Transmitter (Fisher Leveltrol) Receiver for panel mounting (Foxboro) Motor valve. Liquid - 2.2 gpm 1.12 sq. gr., 1/2 - in body, needle stem and seat. Pressure - 55 psig, Temperature - 100°F, Monel trim, steel body, Float, stainless Inconel torque tube	$ 700
1	Liquid Level Controller Recorder. Actuate motor valve controlling steam to reboiler. Transmitter (Fisher Leveltrol) Receiver for panel mounting (Foxboro) Motor valve, steam, 1-in. valve size, Temperature 295°F, Pressure - 50 psig, Stainless steel trim, Iron body, Float: Stainless steel Inconel torque tube.	713
7	Liquid Level Controller Recorder, Actuate motor valve controlling liquid reflux to columns, Transmitter (Fisher Leveltrol), Receiver for panel mounting (Foxboro), Motor valve, Liquid - 3.7 gpm 1.12 Sp. Gr., 1-in. Body, 1/2" orifice, temperature 222°F, Pressure - 55 psig, Monel trim, Monel body, Float: Stainless Steel Inconel torque.	4,983
1	Recording Flow Controller. (Foxboro Stabilog) Actuate motor valve controlling liquid reflux to first column. Transmitter (Republic) Receiver for panel mounting, Motor valve, liquid - 3.7 gpm 1.12 Sp. Gr., 1-in. body - 1/2 in. orifice, Pressure - 55 psig, Monel trim, Steel body	961
9	Temperature indicators at $27.50 (Weston Dial)	250
11	Gage Glasses (say 36" c-c)	847
26	Pressure gages (Steel Bourdon tubes)	572
1	Dry Gas Meter - 35 SCFH Operating, Pressure 0 psig, Temperature 100°F.	83
20 pt.	Temperature Recorder - (4 L & H 6 point recorder)	4,400
24	18-8 TC Wells and Elements	660
1	Liquid level Controller Recorder - actuate motor valve controlling absorber column liquid level	704
1	Flow Controller Recorder - Actuate motor valve controlling stripping gas	963

NO.	ITEM	COST
1	Flow Controller Recorder - Actuate motor valve controlling solvent to absorber	$ 963
1	Temperature Controller Recorder - Control steam to stripping column	770
1	Temperature Indicator - 48 point, Brown Electronic	880
48	18-8 TC Wells & Elements at $27.50	1,320
1	10 Section Instrument Panel	1,100
1	Lot Miscellaneous Instruments	3,190
	MISCELLANEOUS	
1	Supercentrifuge - Remove small amount of solids accumulating in reboiler, Capacity 1 gpm (Sharples)	1,100
1	Steam Generator with all auxiliaries, 50 psig, 4,000 lbs. steam/hr.	11,000

Major Equipment Total	$279,130
Structural Steel, Platforms, Supports	36,000
Pipes, Valves and Fittings	94,000
Transite Siding for Tower Structure	5,000
Electrical Materials	11,000
Insulation	10,000
Winterizing Materials	2,500
Sewers and Drains	600
Paint	600
Foundation	6,000
Freight	4,800
Total Material	$449,630

Direct Erection Labor

Major Equipment	$ 60,100
Structural Steel, Platforms and Supports	42,400
Pipes, Valves and Fittings	100,000
Transite Siding for Tower Structures	8,000
Electrical	16,000
Insulation	15,000
Winterizing	2,800
Sewers and Drains	6,000
Paint	6,000
Foundations	15,000
Total Direct Labor	$271,300
Total Material and Direct Labor	$720,930

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TABLE K

Summary of Cost Estimates for Isotope Separation

	Case I	Case II	Case III	Case IV	Case V	Case VI
Feed Drier	$ 2,420	$ 2,420	$ 2,420	$ 2,420	$ 2,420	$ 2,420
Liquid-Gas Separator	330	330	330	330	330	330
Feed Storage Tank	495	495	495	495	495	495
Byproduct Storage Tank	1,000	1,000	1,000	1,000	1,000	1,000
Overhead Accumulator	440	440	440	440	440	440
Distillation Columns	122,400	76,500	110,000	69,000	148,000	74,000
Absorption Column	2,200	2,200	1,870	1,870	2,200	2,200
Stripping Column	1,100	1,100	1,100	1,100	1,100	1,100
Pumps						
Reflux Pumps	7,920	4,950	7,920	4,950	13,200	6,600
Feed Pumps	1,100	1,100	1,100	1,100	1,100	1,100
Bottom Product Pumps	990	990	990	990	990	990
Reaction Product Transfer Pump	1,540	1,540	1,540	1,540	1,540	1,540
Rich Solvent Pump	660	660	660	660	660	660
Lean Solvent Pump	660	660	660	660	660	660
Blowers						
Overhead Vapor Blowers	52,800	33,000	52,800	33,000	66,000	33,000
Strip Gas Blowers	3,520	3,520	3,520	3,520	3,520	3,520
Heat Exchangers						
Reaction Cooler and Condenser	430	430	430	430	430	430
Overhead Condenser	11,000	11,000	7,700	7,700	11,000	11,000
Reflux Heater	1,320	1,320	1,100	1,100	1,320	1,320
Reboiler	12,100	12,100	9,075	9,075	12,100	12,100
Bottom Product Cooler	132	132	132	132	132	132
Stripper Overhead Cooler	110	110	110	110	110	110
Solvent Heat Exchanger	660	660	660	660	660	660
Rich Solvent Heater	440	440	440	440	440	440

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TABLE K (Continued)

	Case I	Case II	Case III	Case IV	Case V	Case VI
Instruments						
Pressure	$ 540	$ 540	$ 540	$ 540	$ 540	$ 540
Pressure Controller Recorders	9,912	6,182	9,912	6,182	12,364	6,182
Differential Pressure Recorders	3,520	2,200	3,520	2,200	8,800	7,040
Reflux Rotameters	1,892	1,183	1,892	1,183	4,730	3,784
Miscellaneous Rotameters	640	640	640	640	640	640
Liquid Level Controller Recorders	7,800	5,676	7,800	5,676	16,280	17,710
Flow Controller Recorder	2,887	2,887	2,887	2,887	2,887	2,887
Temperature Controller Recorder	770	770	770	770	770	770
Temperature Indicators	250	250	250	250	250	250
Temperature Recorder	4,400	3,300	4,400	3,300	8,800	7,700
Thermocouples and Wells	1,980	1,815	1,980	1,815	2,640	2,200
Temperature Indicator	880	880	880	880	880	880
Gage Glasses	847	616	847	616	1,773	1,926
Pressure Gages	572	506	572	506	616	506
Dry Gas Meter	83	83	83	83	83	83
Panelboard Sections	1,100	1,100	1,100	1,100	1,320	1,100
Miscellaneous Instruments	3,190	2,640	3,190	2,640	4,400	3,520
Miscellaneous						
Vacuum Systems						2,000
Super Centrifuge	1,100	1,100	1,100	1,100	1,100	1,100
Steam Generation	11,000	11,000	11,000	11,000	11,000	19,000
Major Equipment Total	$ 279,130	$ 200,465	$ 259,855	$ 186,090	$ 349,720	$ 236,065*
Structural Steel, Platforms & Supports	36,000	30,000	36,000	30,000	36,000	30,000
Pipe, Valves and Fittings	94,000	76,000	94,000	76,000	117,000	105,000
Transite Siding for Tower Structure	5,000	5,000	5,000	5,000	5,000	5,000
Electrical Materials	11,000	10,500	11,000	10,500	13,500	11,500
Insulation	10,000	6,250	10,000	6,250	10,600	8,250

TABLE K (Continued)

	Case I	Case II	Case III	Case IV	Case V	Case VI
Winterizing Materials	$ 2,500	$ 2,500	$ 2,500	$ 2,500	$ 2,500	$ 2,500
Sewers and Drains	600	600	600	600	600	600
Paint	600	600	600	600	600	600
Foundations	6,000	4,470	6,000	4,470	6,500	6,150
Freight	4,800	4,100	4,700	4,100	5,100	4,700
Total Material	$ 449,630	$ 340,485	$ 430,255	$ 326,110	$ 547,120	$ 410,365
Direct Erection Labor						
Major Equipment	60,100	44,000	53,200	39,500	70,500	50,300
Structural Steel	42,400	32,500	42,400	32,500	42,400	32,500
Pipe, Valves and Fittings	100,000	81,000	100,000	81,000	125,000	112,000
Transite Siding for Tower Structure	8,000	8,000	8,000	8,000	8,000	8,000
Electrical	16,000	16,000	16,000	16,000	19,700	17,200
Insulation	15,000	9,400	15,000	9,400	16,000	12,400
Winterizing	2,800	2,800	2,800	2,800	2,800	2,800
Sewers and Drains	6,000	6,000	6,000	6,000	6,000	6,000
Paint	6,000	6,000	6,000	6,000	6,000	6,000
Foundations	15,000	11.300	15.000	11,300	16,100	15,400
Total Direct Labor	$ 271,300	$ 217,000	$ 264,400	$ 212,500	$ 312,500	$ 262,600
Total Material & Direct Labor	$ 720,930	$ 557,485	$ 694,655	$ 538,610	$ 859,620	$ 672,965*

* This does not include purchase price or any expenses connected with rehabilitating the old columns.

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TABLE L

DETAILED COST ESTIMATE

PREPARATION OF METAL

NO.	ITEM	COST
1	Polymer Storage Tank, 24" ID x 42", Monel	$ 640
1	Polymer Metering Tank, 6" ID x 48", Monel	520
2	Reaction Kettles, 15 Gal. Cap., Dowtherm Jacketed Gear Motor Driven Anchor Type Agitator, Insulated, Inconel	4,800
1	Monomer Dust Filter, 18" ID x 24", Monel	400
1	Polymer Receiver, 8" ID x 12", Monel	50
1	Monomer Scale Tank, 10" ID x 15", Jacketed, Mounted on Scales, Insulated, Monel	235
1	BF_3 Dust Filter, 4" ID x 24", Jacketed, Insulated, Inconel	735
3	$AlCl_3$ Columns, 6" ID x 96", Dowtherm Jacketed in Two Sections, Insulated, Type 304 Stainless Steel, Complete with Dust Traps 6" ID x 48", water Jacketed, Type 304 Stainless Steel	5,780
1	BCl_3 Receiver, 6" ID x 48", Jacketed, Type 304 SS	850
2	BCl_3 Storage Tanks, 24" ID x 60", Internal Cooling Coils, Insulated, Type 304 S.S. One Only Mounted on Scales	3,925
1	BCl_3 Distillation Column, 3" ID x 120", Packed with 1/4" Stoneware Berl Saddles, Insulated, Monel	450
1	BCl_3 Vaporizer, 16" x 36", Equipped with 2 KW Heater, Insulated, Type 304 S.S.	380
1	Hydrogen Purifying Vessel, 12" ID x 36", Packed with Deoxidation Catalyst, electrically heated, Insulated, Type 304 S.S.	1,000
1	Hydrogen Dryer, Model BAC-150 Lectrodryer or Equivalent, Explosion Proof	1,915
1	Norton Type Reduction Apparatus	8,000
1	Polymer Condenser, 5 sq.ft., Monel Internals	700
1	Monomer Condenser, 5 sq.ft., Insulated, Monel Internals	840
1	BF_3 Cooler, 5 Sq.Ft., Inconel Internals	900
4	BCl_3 Condensers, 5 Sq.Ft., Insulated, Type 304 S.S. Internals	3,360
1	Distillation Column Condenser, 5 Sq.Ft., Insulated, Type 304 S.S. Throughout	1,000
1	Distillation Column Reboiler, 5 Sq.Ft., Insulated, Type 304 Throughout	880
1	Hydrogen Heat Exchanger, 10 Sq.Ft., Double Pipe, Insulated, Type 304 Throughout	780
1	Hydrogen Cooler, 20 Sq.Ft., Double Pipe, Type 304 Internals	700
1	Tail Gas Cooler, 25 Sq.Ft., Insulated, Type 304 S.S. Internals	1,200

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DECLASSIFIED

TABLE L (Continued)

NO	ITEM	COST
1	Tail Gas Condenser Assembly Consisting of one Exchanger, 35 Sq.Ft.; One Condenser, 171 Sq.Ft; One Receiver 16" ID x 3'; All Copper Construction, All Enclosed in Cold Box Packed with Rock Wool to Density of 10 lbs/cu.ft.	$ 7,850
2	BCl_3 Pumps, Gear Type, Cap. 1-10 GPH, 1/4 HP Motor	1,700
1	Platform Scale, $AlCl_3$ & CaF_2 Service, Fairbanks Morse No. 1216 or Equivalent. 300 lbs. cap., 1/4 oz. Divisions	75
1	CaF_2 Electric Drying Oven, 19" x 14" x 19" Inside, Freas No. S-64175 Model 134 or Equivalent, with 12 14" x 19" S.S. Trays	650
1	Aluminum Chloride Crusher, 5" x 8" Sturtevent Lab. Roll Mill or Equivalent, Motor Drive	1,820
1	Aluminum Chloride Screener, SWECO Model H-1D-3 18" or Equivalent, with 40 and 70 Mesh Screens	565
1	Product Ball Mill & Classifier, Hardinge Laboratory Dry Grinding Unit or Equivalent	4,465
1	Product Screener, W. S. Tyler Ro-Tap or Equivalent with Screens & Timer	450
1	Magnetic Separator, Stearns 12" Type KB or Equivalent, Complete with Rectifier	980
1	Lot - Weigh Cans, Charging Chutes, Etc.	550
	Laboratory Equipment, Including Four Benchs, Sink, Hood, Etc., and Miscellaneous Apparatus	5,000
1	Air Conditioning Unit, One Ton Capacity, Water Cooled	1,000
1	Packaged Dowtherm Heating & Cooling System, 100,000 Btu/hr. Capacity, Electric Heated, Water Cooled	10,000
1	Process Refrigeration System, Total Capacity 4 Tons at - 100°F, Plus 5 Tons at -20°F Two Stage Freon 22 Cycle, Electric Drive, Water Cooled	12,000
1	Brine Recycling System with Chiller, Circulating Pump, Receiver, Etc.	2,000
	Process Instrumentation	27,460
	Hydrogen and Nitrogen Manifolding Systems	2,425
	Process Piping	25,000
	Structural Steel, Platforms and Supports	1,500
	Electrical Power Distribution & Lighting Including Control System for Norton Reduction Apparatus	29,300
	Process Dust and Fume Exhaust Systems	6,100
	Equipment Foundations	300
	Total Equipment	$181,230
	Freight	1,000
	Direct Erection Labor	105,695
	Total Equipment & Direct Labor	$287,925

DECLASSIFIED

TABLE M

UTILITY AND SAFETY EQUIPMENT

1	Electrical Substation, 1000 KVA, 3 phase 4160 volts primary 220/440 secondary	$20,000
1	Instrument Air System, complete with one 100 CFM Motor Driven Compressor 50 psig discharge, and alumina type air dryer and receiver	9,900
1	Carbon Dioxide Fire Protection System complete with 40 - 75 lb. CO_2 cylinders, piping and automatic controls	10,000
10	Dry Chemical Portable Extinguishers	600
1	Lot - gas masks, air masks, respirators, fire blankets, automatic artifical respiration equipment	1,050
14	Building Ventilation fans, 8 wall type, 6 roof type	5,500
	Total Equipment	$47,050
	Erection Labor (Direct)	19,110
	Total Equipment and Labor	$66,160

TABLE N
SUMMARY OF ESTIMATES
TOTAL PLANT

	Case I	Case II	Case III	Case IV	Case V	Case VI*
Isotope Separation	$ 720,930	$ 557,485	$ 694,655	$ 538,610	$ 859,620	$ 672,965
Metal Preparation	287,925	287,925	287,925	287,925	287,925	287,925
Utility & Safety	66,160	66,160	66,160	66,160	66,160	66,160
Building Rehabilitation	65,000	65,000	65,000	65,000	65,000	65,000
Testing & Cleanup	30,200	30,200	30,200	30,200	30,200	30,200
Field Distributives	199,520	176,030	196,530	174,080	217,330	195,750
Sub-total	$1,369,735	$1,182,800	$1,340,470	$1,161,975	$1,526,235	$1,318,000
Contingency, 10%	136,970	118,280	134,050	116,200	152,625	131,800
Insurance on Plant	15,000	13,000	15,000	13,000	17,000	14,500
Engineering, Procurement, Expediting, Accounting & Overhead	200,000	180,000	200,000	180,000	220,000	220,000
Engineering Startup	25,000	25,000	25,000	25,000	25,000	25,000
Total Cost	$1,746,705	$1,519,080	$1,714,520	$1,496,175	$1,940,860	$1,709,300
Contractor's Fee, 8%	139,740	121,530	137,160	119,700	155,270	136,740
Total	$1,886,445	$1,640,610	$1,851,680	$1,615,875	$2,096,130	$1,846,040*

* Case VI does not include purchase price or any expenses connected with rehabilitating the old columns.

TABLE O

CRITICAL MATERIAL REQUIREMENTS

Alloy	Weight in lbs.
Monel	101,250
Inconel	1,150
Type 304 Stainless Steel	10,700
Copper *	2,100

* Exclusive of electrical requirements

IV DESIGN, PROCUREMENT & CONSTRUCTION SCHEDULE

The overall job schedule covering the design procurement and construction phases of the subject project is graphically illustrated in Figure V. As evident from Figure V this schedule is based upon starting the engineering phase of the project by May 1, 1953 and completing the construction phase by June 1, 1954. It should be noted that this schedule is rather tight and that any appreciable deviation from the scheduled starting date will have an adverse effect on the desired completion date.

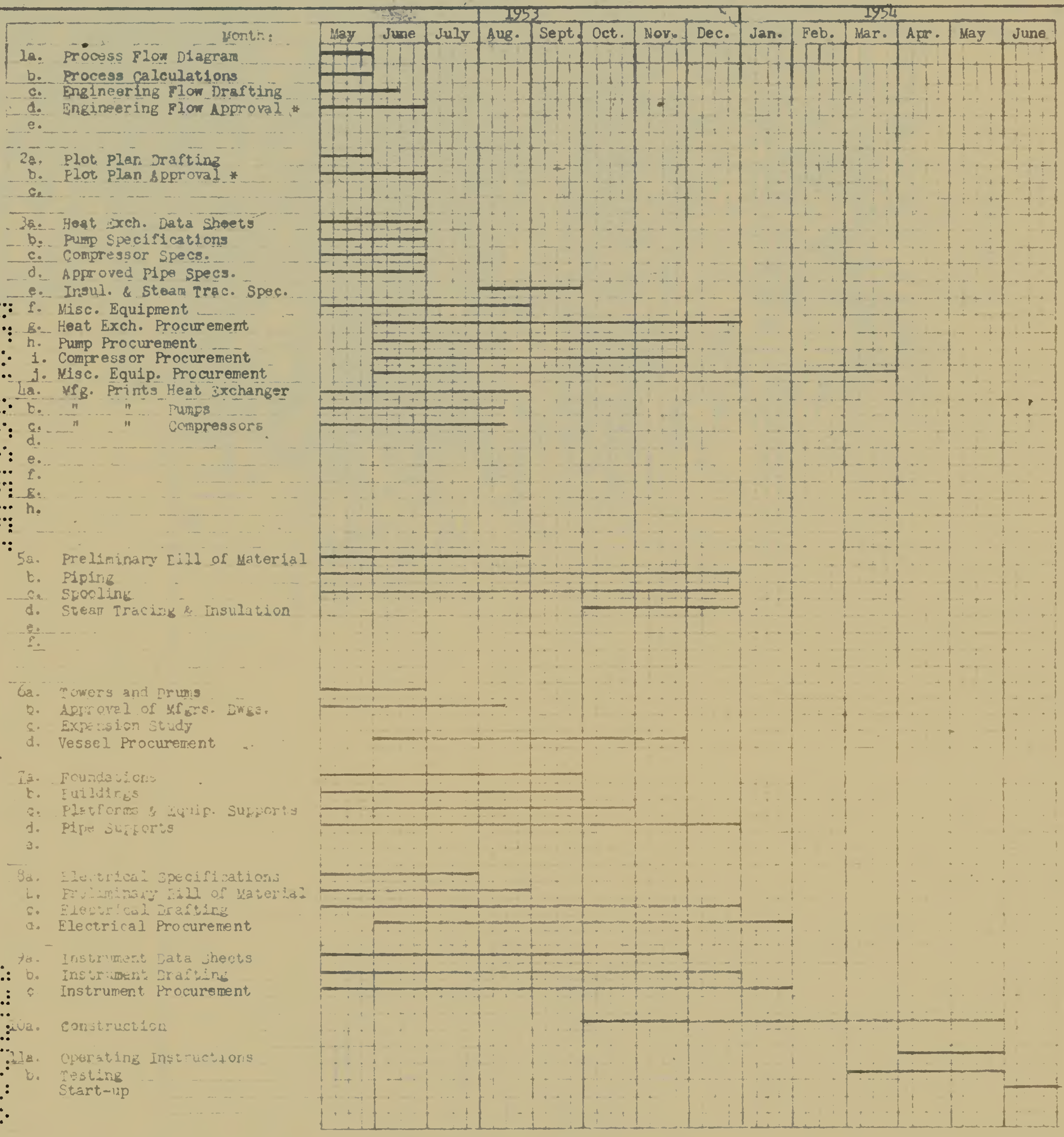
In setting up this schedule it was assumed that the process design used will be one of the cases presented in this report and that relatively little work will be required to finalize the design. On the basis of this assumption we have allowed but one month for the completion of the process design and plot plan layout and another month for the completion of the engineering flow diagrams. During this period the equipment specifications can be determined and should be finalized by July 1. Quotation requests can be started in June and the analysis of quotes, selection of equipment and purchasing can be started in July. On the basis of normal equipment deliveries we should place essentially all orders by September 1 if we expect to get delivery by December and January. It is recognized that some small and special equipment can be delivered at a later date, but the larger components of the plant such as the distillation towers, pumps, blowers, tanks, etc. should be at the plant site by January 1 to allow sufficient time for their erection and the attendant piping, instrumentation, insulation, electrical work, etc., that go with these components. Since we have allowed but six months for our entire procurement schedule it is evident that any delay in starting or completing this phase of the project will of necessity delay the startup date of the plant.

Although we have shown an eight month construction period it should be realized that the bulk of the construction must be done in the four month period from January through April since the major equipment will not be delivered until December or January. We have scheduled construction to begin in October with the thought that the first couple of months could be spent in rehabilitating the existing building, erecting the structure for supporting and housing the distillation towers and installation of the equipment foundations.

Figure VI shows a proposed monthly project analysis which is a breakdown of the scheduled engineering manhours by groups and by months. From this it is seen that the engineering design work is scheduled for completion by January 1 again assuming that this work can be started by May 1.

Figure VII is a graphical interpretation of the engineering design group manhour requirements and reflects only those hours shown for Groups 22 through 27 in Figure VI. For convenience these manpower requirements are plotted in terms of man-months per month instead of manhours.

Figure VIII is a construction force curve and shows the number of construction workers required per month.



* Includes Customer's Approval.

Engineer: E. A. C.

File No. 32-4111

Type Plan A.E.C. Polymer Project.

Remarks

FIGURE V

No.	DATE	REVISION	BY	CHK

THE GIRDLER CORPORATION
LOUISVILLE, KENTUCKY

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SCALE		PROJ. DR.	
DRAWN		CHIEF DR. HCS	4/1/53
CHECKED		ENGINEER EAC	4-1-53

TITLE: JOB SCHEDULE

867-080

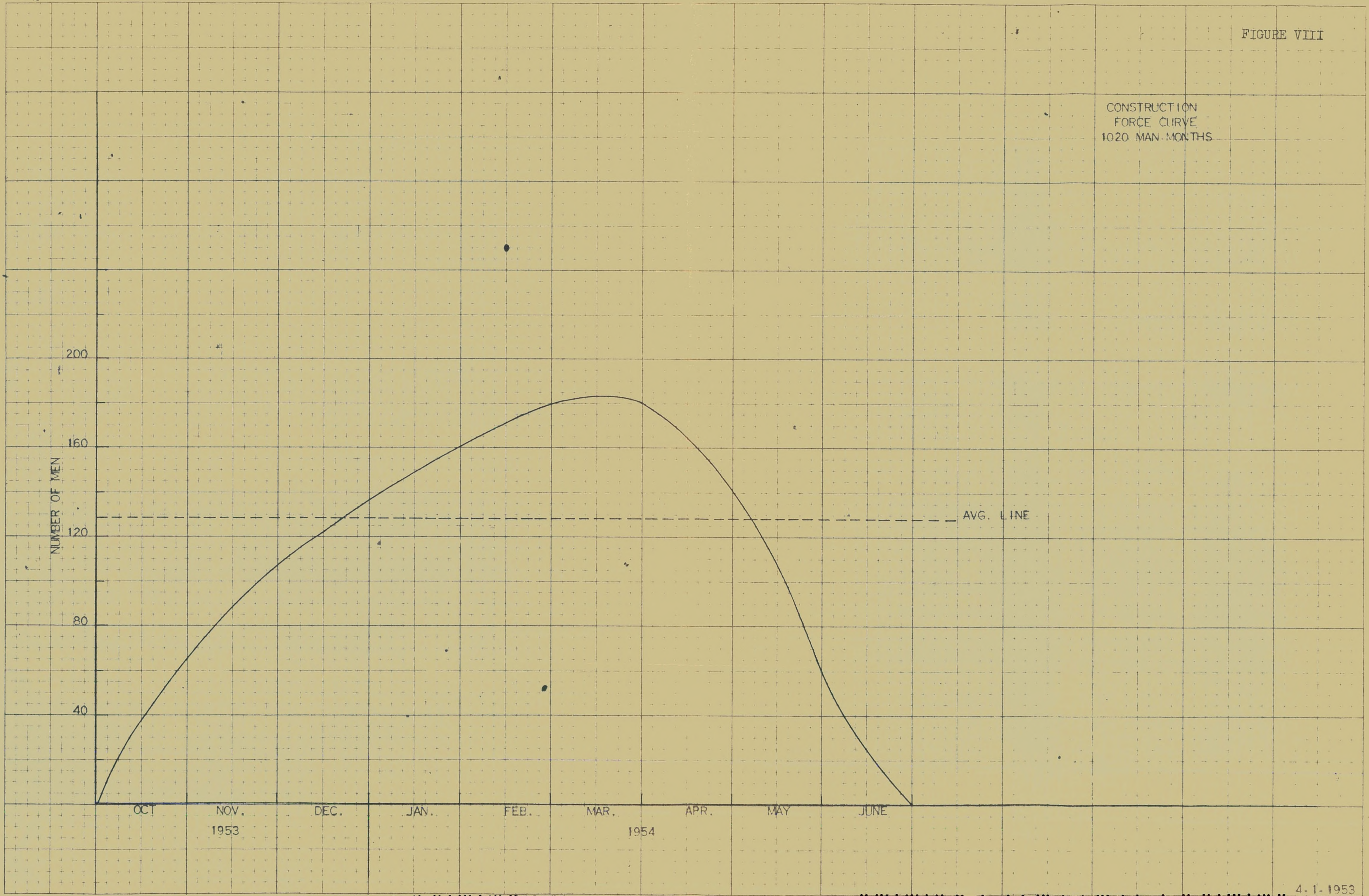
FOR: A.E.C. POLYMER PROJECT

DRAWING NO. B4111-1

REV. 0

BS-203

FIGURE VIII



4-1-1953

867-081

V. SITE EVALUATIONS

A. Summary and Recommendations

As part of the work performed under this contract, a Girdler representative inspected two potential plant sites which had been designated by AEC. Originally a third site at Luckey, Ohio was also to be inspected, but this was later eliminated from consideration by the AEC. The two remaining sites visited were AEC owned properties at Middlesex, New Jersey and Model City, New York (known as Lake Ontario Storage Area). The two sites were compared with respect to location and adaptability of available facilities. No attempt was made to evaluate the effects of such intangible factors as (1) the selection of an operating contractor, (2) possible reasons for dispersal of AEC installations, (3) the suitability of either site for other AEC projects, or (4) the value of either site to other government agencies or private industry.

On the basis of the items considered it would appear that the advantages offered by the Middlesex site outweigh those of the Model City site and the former is hereby recommended. A further discussion of the features at both sites follows:

B. Middlesex, N. J. Site

This site is currently owned by AEC and is operated for them by National Lead Company. The operations now conducted there are due to be discontinued sometime this year. Due to the nature of the materials being

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handled, considerable site decontamination operations would be required if the site were to be sold which could be reduced to a minimum if it remains under AEC health control. The site is relatively small and is located on a public highway. Facilities available are as follows:

(1) Grounds - The entire fenced area of this site is covered with bituminous pavement which appears to be in good condition. It appears to be adequately drained and has a good enough foundation to stand up under heavy live loading. The plot is small enough to be easily patrolled by one or two guards.

(2) Roads and Railroads - A highway gate permits access from the public highway into the paved yard area. The site is served by a railroad spur which runs the full length of the manufacturing building and somewhat beyond.

(3) Manufacturing Buildings - The main plant is a two story steel structure faced with brick. It is approximately 252' x 60' x 23' high (two equal height floors) and encloses a floor area of 30,900 square feet. The ground floor is a 6" reinforced concrete slab poured on compacted shale fill which would be capable of supporting most of the indoor process equipment presently contemplated. The second floor and roof are of wood construction which would permit easy alterations for installing any tall equipment required. The building is adequately heated with low pressure steam unit heaters and is provided with a wet sprinkler system throughout. Additional

features include a full length railroad loading dock, a single truck loading dock and a freight elevator which serves the railroad dock as well as both floors.

The building at present contains some processing equipment which would have to be removed before a new operation is installed. Most of this equipment would be relatively easy to move and could be stored elsewhere on the site awaiting final disposal without interfering with new operations. In order to reduce the contamination it would probably be necessary to scrub the walls and floors but further measures are not deemed necessary by AEC personnel.

In addition to the main plant there is a 1980 square foot cinder block thaw house which would probably not be required for the new operations.

(4) Auxiliary Buildings - In addition to the manufacturing buildings listed above the following auxiliary buildings are available.

a. Administration Building - This is a modern cinder block building with a reinforced concrete roof containing 4020 square feet of floor space. Facilities include two locker rooms, a lunch room and a laundry as well as the administrative offices. It is steam heated throughout. The front door is available from the street so that the entrance and telephone switchboard can be operated by a single guard.

b. Quonset Storage Building - This corrugated steel structure contains 10,900 square feet of area. There is no heat or light in this building.

c. Garage - This is a six vehicle storage and maintenance structure constructed from wood and containing 2880 square feet. It is heated and equipped with light and power outlets.

d. Boiler House and Machine Shop - This building is located adjacent to the main plant and is constructed of brick. Its 1755 square feet of floor space is divided approximately equally between the boiler room and a machine shop. Each room has approximately 15' to 20' headroom.

The boiler room contains two small packaged oil fired boilers, used for space heated of the other buildings, as well as oil and feedwater pumps. An outdoor storage tank has approximately 12,000 gallons fuel oil capacity. Adequate room is available for installing larger boilers in place of the present ones.

The machine shop contains a collection of machine tools that is used for maintenance and which could remain at the site.

(5) Utilities and Drainage - The following utilities are available at the site.

a. Electric Power - Three phase 4160 volt power enters the plant and is reduced to 110-220 volts in 3-50 KVA transformers.

b. Water - City water enters the site in a 6 inch main at a pressure of 80 to 100 psig and a maximum summer temperature of 75°F.

c. Fuel - A 1 1/4" city gas line enters the plant where it is used for the clothes dryer in the laundry. Number 4 oil is used in the boilers.

d. Drainage - Plant effluent is gathered in a 24" sewer which empties into a ditch leading to a creek outside the property line.

C. Model City, N. Y. Site (Lake Ontario Storage Area)

This site was formerly an Ordnance Works which is currently owned by the AEC. Some small operations are being conducted in a few of the buildings which could be continued without interfering with any new operations. No decontamination of any of the buildings considered would be required. The site is approximately 1000 acres in area and is remote from other industrial or residential areas. Facilities available are as follows:

(1) Grounds - The area inside the fence line consists mostly of open fields with some wooded areas. As the area is quite large it would be hard to patrol adequately with a small guard force.

(2) Roads and Railroads - The area is adequately served with hard surfaced roads and a system of railroad spurs. The spurs have only 85 lb. rails, thus a light switch engine must be used to move cars in and out.

(3) Manufacturing Buildings - Three buildings were considered for the main manufacturing operation. They are discussed in order of their desirability. Others inspected, which did not appear usable for various reasons, include the Water Treatment Plant and the TNT processing buildings.

a. Combined Shops Building - This is a wooden structure approximately 80' x 400' with about 14' headroom up to the chord of the wooden roof trusses and about 20' to the roof. The floor is a concrete slab at ground level. Power and water are available in small quantities at the building but heat would have to be supplied. A wet sprinkler system protects the whole building. A railroad spur enters one end of the building. It would be possible to house the second stage of the process within this building by partitioning off the desired length and supplying operating platforms at elevations near the roof. There is adequate free area adjacent to the building for erecting the first stage equipment, or it could be arranged to project through the roof.

b. Box Factory. This is a wooden structure with corrugated steel siding and brick fire partitions approximately 70' x 240' overall. The floor is concrete at loading dock elevation. A railroad spur and deteriorated wooden dock run the length of the building on one side with truck loading docks on the other. Power and water are available in small quantities and at least part of the building is protected with a sprinkler system. No heat is presently available. This building could be used to house the project in a similar manner to the Combined Shops Building.

c. Boiler House - This is a structural steel building 112' x 96' in area with three floors at various elevations giving it a total height of approximately 60' to the eaves and 75' to the peak of the roof. The siding is coated corrugated metal. The floors are reinforced concrete. The building was designed to hold three large coal burning boilers, since removed, and is not readily adapted to other operations without considerable alteration. Light and water could be made available but heat might become a major problem in a building of this size and construction.

d. Summary - From the point of adaptability the Combined Shops or the Box Factory appear more attractive than the Boiler House. As the latter is not high enough to contain the towers presently contemplated for the first stage, the extra height affords very little advantage although it might be desirable to locate some equipment on the second floor. As the Combined Shops building appears to be in better condition and is located nearer the office and service buildings, it is felt to be the most desirable at this site.

(4) Auxiliary Buildings - In addition to the manufacturing buildings listed above the following auxiliary buildings are available.

a. Office Building - This is a remodeled wooden structure with asbestos shingles containing 4000 square feet of floor space. Offices, locker rooms, a lunch room and laundry equipment are located in this building.

b. Storage Buildings - There are a number of small wooden storage buildings located near the office building which would be available for miscellaneous purposes if required.

c. Garages - Two garages are available. One, used for vehicular storage and repairs, contains over 4000 square feet of floor space and is heated by a low pressure steam unit heater. The other is a storage garage with over 11,000 square feet. Gasoline pumps and buried storage tanks are available.

(5) Utilities and Drainage - The following utilities are available at the site.

a. Electric Power - Three phase, 4800 volt power enters the area and is reduced to 110-220 volts in transformers with a present capacity of 250 KVA.

b. Water - A 10" line from the Niagara Falls city water system could supply 500 gpm at 74°F maximum temperature according to the water company. The present usage is considerably less, although Bell Aircraft, which uses water from this line, are presently using all they can get. Present pressure is 40 to 60 psig.

c. Fuel - No gas is available. Number 2 oil is used in the boilers.

d. Drainage - The plant area is drained by ditches and creeks leading to Lake Ontario. A sewage disposal plant is available but not in use.

D. Comparison of Sites

In comparing the two sites the following points have been considered:

(1) Location Considerations

a. With respect to sources of raw materials and process equipment and point of use of manufactured product there is very little choice between the two sites.

b. There seems to be very little choice between sites as far as labor supply is concerned. Construction labor rates are slightly lower at the Model City site (See Table p).

c. In relation to other AEC operations Middlesex would have a definite advantage due to the proximity of the New Brunswick laboratories for unusual analytical work. This could be of extreme importance at startup time or times of process upsets. It could also reduce the laboratory facilities required at the site to a very simple setup. Good communications and transportation to the New York Operations Office exist.

d. With respect to security considerations, Model City is more remote but, due to its large area, would be more difficult to patrol adequately.

e. Both sites have adequate transportation, but Middlesex is more conveniently located with respect to the transportation of operating personnel to and from work.

f. Middlesex is slightly favored with respect to climate as the winters would not be as severe as at Model City. This could have an effect on the construction schedule as much of the work will have to be done in the winter.

g. Since there will be no undesirable effluent from the process there is no need to locate it remotely.

(2) Physical Considerations

a. The size and compactness of the Middlesex site would be conducive to more efficient operation and easier to guard and maintain than the Model City site. There is more than adequate room at Middlesex for this project and any future expansion of production, whereas, the site might be too small for other AEC projects which could use Model City to advantage.

b. The existing manufacturing building at Middlesex is a more permanent type construction and would be more readily adapted to some phases of the operation which could be performed on two levels to advantage.

c. The auxiliary buildings at Middlesex are more modern and permanent in nature and are located more conveniently to the manufacturing building. The boiler house and machine shop at Middlesex are definite advantages.

d. Rehabilitation of either site would not require any major work but, in general, it appears that the extra work that would be required in removing the equipment and decontaminating the Middlesex site would be offset by the extra work that would be required to add heating and shop facilities to the Model City site.

(3) Utilities

The present availability of utilities is about the same at both sites. It would appear that expansion of the electric power facilities could be accomplished without major expense at both sites if required.

TABLE P

Construction Labor Rates

	Middlesex (1)	Model City (2)
Pipefitters	$ 3.15	$ 2.90
Millwrights	2.95	2.95
Carpenters	2.90	2.85
Painters	2.90	2.52
Structural Steel Workers	3.45	2.925
Electricians	----	2.90
Operating Engineers	3.40	----
Bricklayers	----	2.90
Cement Finishers	----	2.90
Laborers	2.15	2.10

Sources of Information:

(1) Decisions of Construction Industries Stabilization Committee in same area.
(2) Building Trades Council, Niagara Falls, N. Y.

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APPENDIX A

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867-095

DECLASSIFIED

Report No. T8.10-1-1

~~SECRET~~

THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

THE PRODUCTION OF ELEMENTAL BORON. LITERATURE REVIEW.

March 27, 1953

Report by:
Kenton Atwood

~~SECRET~~

Sentence Summary

Chemical Abstracts, Volumes 1 to 46, were reviewed.

867 096

DECLASSIFIED

I. INTRODUCTION:

In connection with Contract No. AT(30-1)-1506 (Job No. 32-4111, A-407) for the Atomic Energy Commission, a brief literature search on methods of producing elemental boron was made. Chemical Abstracts, Volumes 1 to 46, were reviewed. The purpose of this report is to make abstracts of the more recent literature readily available.

II. SUMMARY OF PREVIOUS WORK:

In Volume 5, Division III of the National Nuclear Energy Series, Manhattan Project Technical Section, the literature on this subject is reviewed. The early work by Wöhler and Deville and others is covered, as well as important work done prior to 1944.

III. RECOMMENDATIONS:

Unavailable original references should be obtained and studied, and the bearing of this literature on the subject contract should be considered.

IV. DISCUSSION:

The problem of producing pure, especially pure crystalline boron, has been very difficult, and many products which have been thought to be boron have actually been borides. This is particularly true of boron prepared by reduction of boron compounds with metals or carbon. Apparently the purest boron has been made by either the decomposition of boron halides or their reduction with hydrogen.

The literature cited in this report may be divided into five categories:

1. Reduction of Boron Compounds with Metals and Other Solid Reducing Agents.

   References 2, 4, 5, 8, 10, 11, 12, 17, 18, 25, 28, 33, 38, 41, 44.

   Mg, Fe, Al, Zn, Na, C, and LiH have been used.

2. Reduction of Boron Halides with Hydrogen. References 1, 6, 7, 8, 9, 12, 16, 24, 30, 32, 33, 36, 37, 40.

   BCl_3 has usually been used at above 1000°C.

3. Electrolytic Reduction - References 13, 14, 19, 21, 22, 23, 26, 42, 43.

   This method has generally given an impure product, but recent patents (42, 43) claim a cell capable of yielding very pure crystalline boron.

4. Thermal Decomposition of Boron Halides - References 15, 20, 27, 29, 39.

   BBr_3 is usually used.

5. Production of Boron from Boron Hydrides - Reference 34.

   BH_3 (?) is said to yield B by reaction with H_2. This abstract may be in-error.

6. General - References 3, 31, 32, 35.

   These are descriptive papers on the preparation and properties of boron.

REPORT BY: Kenton Atwood DATE: March 27, 1953

READ AND UNDERSTOOD BY: W. M. Kiely DATE: March 27, 1953

jc

LITERATURE CITED

1. C.A. 4, 155^3 (1910) "The Preparation at High Temperatures of Some Refractory Metals from Their Chlorides." J. N. Pring and W. Fielding. J. Chem. Soc. 95, 1497.

   The conditions for the separation of W, Mo, Cr, Si, and B from their chlorides were studied. The apparatus was a 2-liter glass flask in which a 5 mm. carbon rod 9 cm. long was held between water-cooled brass electrodes provided with graphite end-pieces. The flask could be evacuated by a Töpler pump and the metallic chloride vapor admitted, or the vapor mixed with H could be passed through the apparatus. The black-body temp. was measured by a Wanner pyrometer. Boron: $BCl_3 + H_2$ in excess at atmospheric pressure deposits B from 1500 to 1750°, and B_6C up to 2150°. At 2200°, a complete coating of B_6C could not be obtained on the rod, but free B and B_6C deposited like soot on the water-cooled electrodes. Above 2000° B appears to exert a catalytic effect in converting the C into graphite. Similar results were obtained with BCl_3 and a small amount of H at 1/2 atm......

2. C.A. 4, 1132^3 (1910) "Preparation and Properties of Pure Boron". E. Weintraub. Trans. Am. Electrochem. Soc., 16, 165-84.

   The reaction between B_2O_3 and Mg is shown to give, under the most favorable conditions, 82.5 to 94% B with varying amounts of Mg, O and Fe as impurities. This reaction was found to give the best results when carried out in an elec. furnace or in a large mass where the interior was heated quite high by its own reaction. This gave a product practically free from Mg. Experiments showing the existance of a suboxide $B_{15}O_2$ or possibly B_7O are described. The production of absolutely pure B was arrived at by passing an arc discharge through a mixture of BCl_3 and H, the latter in large excess. The use of a. c. of high potential from water- or air-cooled Cu electrodes was found to eliminate practically all contamination from electrodes. The B, being a solid, is being continually thrown out upon the electrodes and sides of the glass or Cu tube used, and as the deposit grows, very often fuses into beads and drops off. Analysis of the fused lumps show 99.8-100% B. A 30% theoretical yield is considered good. BCl_3 can be condensed from the escaping gases and used over again. The m. p. is given at from 2000 to 2500°. Its fracture is conchoidal and in hardness is inferior only to the diamond. It is also inferior to the diamond in toughness. Its most interesting property is its elec. cond. which increases about 2,000,000 times from room temp. (23:) to dull red, a rate of increase unknown in any other element. Use of this exceptional property is suggested as a motor-starting device, wireless detector, or sensitive pyrometer. Between pure B and B containing 8% C there is an interesting region in which almost any desired negative temp. coeff. of resistance may be obtained. A trace of B added to C on the other hand changes the latter's negative temp. coeff. of resistance to a positive one, or, as the author says, "chemically metallizes" it.

3. C.A. 5, 2221^3 (1911) "The Properties and Preparation of the Element Boron". E. Weintraub. J. Ind. Eng. Chem., 3, 299-301.

   (No abstract given)

4. C.A. 5, 2780[3] (1911) U.S. 997,879, July 11. E. Weintraub, Schenectady, N. Y. Assignor to General Electric Co.
Making boron by reducing B_2O_3 with Mg, grinding the product with H_2O or HCl and removing the lighter part of the suspension by fractional decantation. The patent also covers heating impure B in vacuo (preferably to about 1200°) to dissociate and drive off the impurities and render the B conducive of electricity, and then fusing it as anode in a Hg vapor arc so that it may be used in incandescent lamps, etc.

5. C.A. 6, 1273[1] (1912) U.S. 1,019,569, March 5. E. Weintraub. "Producing Boron and Boron Compounds".
(No abstract given)

6. C.A. 6, 1406[5] (1912) Brit. 25,033, Oct. 27, 1910. E. Weintraub.
Boron and zirconium are obtained by the action of electric arcs on mixts. of vaporized halogen compds. with H. Form of app. shown.

7. C.A. 7, 575[2] (1913) U.S. 1,046,043, Dec. 3. E. Weintraub.
Producing boron by passing H and a B halide, e.g., chloride, directly through an elec. arc.

8. C.A. 7, 2022[3] (1913) "Boron, Its Properties and Preparation". E. Weintraub. J. Ind. Eng. Chem., 5, 106.
At ordinary temps., B possesses a high sp. resistance dropping from 77500 ohms, at 27°, to 4 ohms at 600°. This drop is due to an unprecedented neg. temp. coeff. which causes the cond. to double per 17° rise in temp. at ordinary temps., and per 80° rise in the neighborhood of 600°. A trace of dissolved substance, e.g., 0.1% of C, increases the cond. many fold, at the same time decreasing the temp. coeff. which still remains neg. This effect is of great practical value. Breakdown curves are given which show that B is similar to other negative temp. coeff. substances in this respect. B is prepared quite pure and in large quantities by heating B_2O_3 with Mg or alkali metals. The resulting mixture of B and Mg boride is purified by B. out the impurities in a Hg arc furnace in an indiff. atm. A purer form of B is obtained by reducing BCl_3 with H in contact with an incandescent surface.

9. C.A. 7, 3926[1] (1913) U.S. 1,074,672, Oct. 7. E. Weintraub.
Boron made by reaction of boron chloride and hydrogen, by use of the elec. arc, the product being black, harder than sapphire, m. above 2000°, of very high negative temp. resistance coeff., electrically conductive, oxidizable to B_2O_3, chem. inert to Cu and combining directly with Cl to form a volatile colorless liquid.

10. C.A. 9, 276[9] (1915) "Magnesium Boride and Amorphous Boron". R. C. Ray. J. Chem. Soc. 105, 2162-8 (1914).
When B_2O_3 is heated with Mg powder only one boride, Mg_3B_2, is obtained. When this is heated to a higher temp. a mixt. of amorphous and cryst. B results. The amorphous B always contains O and appears to be a soln. of a lower oxide of B and of MgO in elementary B. On heating Mg with cryst. B no reaction takes place, but with the so-called amorphous B a mixt. of Mg_3B_2 and MgO is obtained. No other boride is formed.

11. C.A. 11, 3183^4 (1917) "The Preparation in a Pure State of Highly Reactive metals and Alloys". Emil Podszus. Z. anorg. allgem. Chem. 99, 123-31 (1917); J. Chem. Soc. 112, II, 373-4.

For the prepn. of Ti and Zr, a steel bomb was used, closed by a strong steel screw and sealed with molten Pb. The reduction mixt., consisting of Na and $TiCl_4$ or K_2ZrF_6, was introduced in an atm. of H or CO, several clean Fe balls being added. The bomb being closed, the whole was revolved for 20-40 hrs. at a temp. of 200° to bring about an intimate mixt. Heating strongly for a few min. starts the reaction. When a large excess of Na is used, vapor may escape through the Pb seal. The bomb was cooled from the top downwards so that the Pb may be solid before the pressure falls. The elements were obtained in a minutely cryst., highly reactive form, Ti being 99.7%, Zr 99.3%, pure. The method fails to give pure B. App. is described for the prepn. and purification of BCl_3. Reduction with Na, even in a vessel of pure boron nitride elec. heated by a resistance spiral of B and boron carbide, yielded only a black powder which will not weld into a compact mass. Fe was found to give the best results. Wire, prepd. by drawing down Kahlbaum's pure Fe, was wound on a frame made of BN, and heated by means of a resistance tube of B and boron carbide enclosed in a large glass vessel with Hg seals. The leading-in wires were of W. After filling with H the furnace was heated to redness to remove any trace of O, and H was then expelled by filling with BCl_3. Most of the reduction takes place at about 800°, and the temp. is then raised gradually to 1700°. A porous mass of pure B was thus obtained which becomes denser on prolonged heating in BCl_3. Compact B thus prepd. has an appreciable conductivity and is very infusible, an arc struck between B poles showing no trace of fusion unless Fe is present. The wires may be heated elec. to bright redness without injury.

12. C.A. 12, 2504^7 (1918) "Preparation of Amorphous Boron". Wilhelm Kroll. Z. anorg. allgem. Chem. 102, 1-33 (1918); J. Chem. Soc. 114, II, 109.

An account of numerous expts. on the reduction of B compds. Al is unsuitable. Na yields mixts. of the lower oxides of B mixed with boride. Ca produces only borides. Mg may be used for the reduction of H_3BO_3, but the product contains more than 3% Mg in the form of insol. boride. The halogen compds. of B can be reduced by K, Na, Mg and Al; in each case borides of the metal are formed as well as free B. The purest B is obtained by the reduction of BCl_3 with H in the high-tension arc. Red P does not reduce H_3BO_3. When H_3BO_3 is heated with Mg_3N_2 a boron nitride, probably B_3N, is produced. Boron nitride, BN, can be conveniently prepd. from H_3BO_3 and $CaCN_2$. When BCl_3 is passed over red P in the presence of O, a phosphate, $2B_2O \cdot P_2O_5$, is formed. Other phosphates appear to exist. The original contains details as to analytical processes regarding compds. of B.

13. C.A. 15, 3034^5 (1921) "Boron Manufacture". G. Constant and V. Raisin. Brit. 162,252, Apr. 22, 1921.

B is produced by electrolysis of fused boric acid made conductive by the addition of a suitable substance such as borax. Both electrodes may be metallic or the anode may be of retort carbon. CO and CO_2 formed in the latter case assist in the operation. The process is carried out in a closed vessel having an outlet pipe for gases. The vessel may be of insulating material or of metal and in the latter case forms the cathode. The cables pass through the wall of the vessel or through the cover. B so produced may be used as a reducing agent in metallurgy.

14. C.A. 15, 3034^6 (1921) "Manufacture of Boron". G. Constant and V. Raisin; Brit. 162,655, Apr. 26, 1921. Addition to 162,252.
B is obtained by electrolysis of a mixt. of fused boric acid with a saline or basic electrolyte such as NaCl or an alkali borate. The boric anhydride itself may be replaced by an alkali or other fusible borate or mixt. of borates.

15. C.A. 16, 1053^2 (1922) "The Preparation of Boron by the Dissociation of Boron Bromide". Friedrich Meyer and R. Zappner. Ber. 54B, 550-5 (1921).
The authors first prepare pure BBr_3 by dropping Br on fairly pure B and redistg. the product under reduced pressure, thus removing the excess Br and leaving a very good product. The BBr_3 is then heated in a moisture-free app. in such a way that the BBr_3 vapor is subjected to the action of an elec. arc, Cu electrodes and a difference of potential of 80,000 to 100,000 v. being used. Such action dissociates the BBr_3, leaving pure B. To make the dissociation more complete in some cases pure Cu was added, which also combined with the Br and aided in the dissociation. Such Cu as well as Cu coming from the electrodes was removed with KCN soln. Analysis shows the product to be about 99.8% pure.

16. C.A. 17, 3116^6 (1923) "The Element Boron". A. H. Warth. Bull. Maryland Acad. Sci. 3, No. 3, 8-9 (1923).
A new method for the prepn. of relatively pure B consists in the reaction of BCl_3 with H in the presence of a glowing W filament at 1300-1850°. The B deposits on the W, from which it is easily stripped. It is harder than sapphire, and brittle; it has a high tensile strength. The sp. resistance is 9×10^5 ohms per cm.^{2} at 26°. This drops in half for 12-17° increase in temp. The d. is 2.3; the coeff. of expansion is approx. 2.0.

17. C.A. 17, 3580^3 (1923) "Refining Copper; Boron". British Thomson-Houston Co., Ltd. Brit. 193,894, Oct. 1, 1921.
B, mixed or not with boric acid, is obtained by reducing a borate such as fused borax, or boric acid with Al, excess of the boric acid and usually an excess of the borate being employed. The powd. materials are mixed and heated to 700°, when reaction occurs, causing the temp. to rise to 900°. The product on cooling sets to a block, and is powdered. About 0.5% of the B compn. is added to Cu before casting, to remove impurities in the form of a slag.

18. C.A. 19, 1999^4 (1925) "The Zinc Arc as a Reducing Agent". Alfred Stock, Arnold Brandt and Hans Fischer. Ber. 58B, 643-57 (1925).
An app. is described in which an arc is struck between Zn electrodes or Zn and C electrodes. With 6-mm. Zn rods a 2-hr. exposure of 400 cc. CS_2 to 4-5 amp. 110 v. d.c. caused a loss of 5.2 g. Zn on the anode and 7.2 g. on the cathode, with the formation of 11 mg. C_3S_2 per g. Zn volatilized. In a bath at -80° with a 6-mm. Zn anode, a 12-mm. C cathode and 400 cc. CS_2, in an hr. only 0.4 g. Zn was lost, and 150 mg. C_3S_2 per g. Zn was formed. With a.c. no C_3S_2 was formed although considerable Zn was lost. $SiCl_4$ in absence of oxygen or moisture, cooled externally to -80°, with 20-24-v. d.c. and 4 amp. produced Si_2Cl_6. The electrode was converted to $ZnCl_2$. In air a mixt. of 30-40% Si_2Cl_6 and 70-60% Si_2Cl_6O was formed PCl_3 (method of purification given) 50 cc in 3/4 hr., with a 12-mm. Al cathode and a 6-mm. Zn anode, at 4-5 amp. cooled to -75°, volatilized 0.8477 g. Zn and 0.0117 g. Al. The reaction was chiefly $2PCl_3 + 3Zn = 2P + 3ZnCl_2$; partly $2PCl_3 + Zn = P_2Cl_4 + ZnCl_2$. With BCl_3 about 1.5 g. Zn was lost. Solid B and some B_2Cl_4 were formed.

19. C.A. 21, 3563^5 (1927) "New Process for the Preparation of Boron" L. Andrieux. Compt. rend. 185, 119-20 (1927).

Electrolyzing a molten bath having the compn. $2B_2O_3 + MO + MF_2$ gives at the cathode either the metal M or a boride of this metal mixed with a greater or less proportion of B. In the first case only the oxide MO is decompd., while in the second, the metal M reduces the B_2O_3 of the bath, liberating B, which combines partly or wholly with M. On carrying out the electrolysis at 1000-1200° with baths yielding metals which can reduce B_2O_3 A. found: (1) with alkali borate and fluoride the results are similar to those obtained hitherto with $Na_2B_4O_7$ or $K_2B_4O_7$ alone (low yield of very impure B); (2) with alk. earth metals or earth metals the cathode deposit consists mainly of the boride of the metal, but with Mg the product may consist almost entirely of B. Electrolyzing at 1100° a bath consisting of $2B_2O_3 + MgO + MgF_2$ in a graphite crucible (as anode) gives a cathode deposit of B agglomerated by part of the solidified electrolyte. Pulverizing and treating the deposit with HCl gives a residue of amorphous B, which, after drying in vacuo at 110°, contains up to 95% pure B; it may be further purified by fusing in dry H according to Weintraub. The process can be made continuous, as the cathode can be withdrawn from the bath and replaced without fear of igniting the B. The current efficiency can reach 95%.

20. C.A. 22, 196^1 (1928) "Boron" Naamlooze Vennootschap Philips' Gloeilampenfarbrieken. Brit. 264,953, Nov. 9, 1925.

B bromide or other B halide is dissocd. by being brought into contact with a heated metal core such as an elec. heated W wire upon which the B is deposited in coherent form. Liberated Br may be bound by Hg in the reaction vessel.

21. C.A. 23, 4893^1 (1929) "Electrolysis of Metallic Oxides Dissolved in Fused Boric Acid and in Fused Borates (Tungsten, Molybdenum, Zinc)." Lucien Andrieux. Masson et Cie, Paris, France, Thesis, 1929.

A. found that in the electrolysis of borax, Na metal is the primary product. This Na thus liberated reacts with the B_2O_3, resulting in amorphous B at the cathode. Thus, the electrolysis of a metal borate is a means of liberating the metal of this borate. The electrolysis of K and Li borate likewise produces B. Electrolysis of borates of the alk. earths results in a product composed of amorphous B and boride of the alk. earth metal. The borates of Ce and Mn produce borides of these 2 metals. Mg borate results in a very pure B. This reaction was studied in detail. The addn. of MgF_2 facilitates the reaction. A graphite crucible was used and the charge consisted of B_2O_3, MgO and MgF_2. The method is much better than the older method of Moissan. The electrolysis of tetraborate of Ca results in a mixed product of B and boride of Ca. With Mg there is a tendency to form pyroborates. These borates gather around the cathode in the shape of a solid, cryst. ball surrounded by the bath, which is perfectly fluid at 1000°. This is a new and curious phenomenon. To obtain the boride of a metal A. electrolyzes a mixt. of borate and of fluoride of the metal. In this way 17 borides have been prepd., 10 of which are new: CaB_6, SrB_6, BaB_6, ThB_6, Zr_3B_4, Cr_3B_2, MnB, and the new borates CeB_6, LaB_6, NdB_6, GdB_6, YB_6, ErB_6, YbB_6, TiB_2, VB_2, UB_4. Among the metals produced are Zn, W and Mo. Zn can be obtained by the electrolysis of the oxide of Zn dissolved in a bath of B_2O_3 or of borates to which have been added fluorides or other salts to lower the fusing temp. of the bath. W and Mo can be obtained by dissolving the trioxide of the metal in the bath of borate and fluoride with an addn. of oxide of Zn.

22. C.A. 24, 5238^1 (1930) "The Electrolysis of Metallic Oxides Dissolved in Fused Boric Anhydride or Borates. New Methods for the Preparation of Amorphous Boron, Borides and Some Metals". Lucien Andrieux. Ann. chim. (10), 12, 423-507 (1929)
See C.A. 23, 4893.

23. C.A. 25, 4474^6 (1931) "Boron and Borides". Jean Lucien Andrieux. Fr. 37,559, June 17, 1929. Addn. to 638,345.
B is obtained by electrolysis of a bath contg. B_2O_3, MgO and MgF_2. Metal borides are prepd. by electrolysis of a bath contg. the borate and the fluoride of the metal, or by the electrolysis of baths composed of mixts. of borates and fluorides of alkalies, alk. earths or earths and the oxide of the metal the boride of which is desired. The prepn. of TiB_2, VB_2, TaB_2, UB_4 and the borides of Cr, W, Mo, Zr, Ta, Fe and Ni is referred to.

24. C.A. 26, 663^7 (1932) "Crystallized Boron" L. Hackspill, A. Stieber and R. Hocart. Compt. rend. 193, 776-8 (1931).
Pure B was obtained by passing a high-frequency spark through a mixt. of H_2 and BCl_3 vapor. Spectrum analysis showed it to be crystalline and probably of a hexagonal system.

25. C.A. 26, 4922^6 (1932) "Boron". Andre Marinot. Fr. 725,789, Jan. 10, 1931.
B is obtained by reducing boric anhydride with Mg. The fused mass is enriched by the addn. of borax and an equal wt. of Al.

26. C.A. 28, 3008^6 (1934) "Boron" Jean L. Andrieux. Ger. 593,425, Feb. 26, 1934.
A fused mixt. of Mg borate (or B_2O_3 and MgO) with a fluoride is electrolyzed. A suitable mixt. contains B_2O_3 140, MgO 40 and MgF_2 62 parts, and may be treated at 1100° and 10-15 v.

27. C.A. 28, 5011^7 (1934) "Production of High-Melting Metals by Thermal Dissociation of Their Compounds". A. E. van Arkel. Metallwirtschaft 13, 405-8 (1934).
Metals can be produced in very pure form by heating one of their compds in an evacuated vessel, providing the compd. will dissociate into the metal and gas at a temp. below the m.p. of the metal. In this method the metal is not melted and does not come in contact with impurities. W can be prepd. by heating WCl_6 in an evacuated Pyrex tube to about 300°, which causes it to volatilize. In the upper part of the tube a W wire is heated electrically to 1400°. This temp. causes the WCl_6 to dissociate, pure W is deposited on the wire, which grown uniformly, and Cl gas is liberated. The Cl combines with W powder which has been placed in the tube and the process continues until the W powder is used up. Wires of several mm. diam. can be prepd. in this way. By similar processes Si, Cb, Ta, Mo, and Re can be produced from their chlorides, B from BBr_3, Be, Cu, Ti, Zr, Hf, Th, V, Cr and Fe from their iodides, Ni from Ni carbonyl and Pt from Pt carbonyl chloride. The temps. to which the compds. and the metallic wires should be heated and the means for removing the gas formed are given. It is also possible to produce some alloys and compds. by this method.

28. C.A. 28, 5030^8 (1934) "Metals and Metalloids". Karl Mitterbiller-Epp. Fr. 763,124, Apr. 24, 1934.
These are prepd. by causing their oxides, silicates or carbonates and C or CO to react with a halide of the corresponding metal or metalloid at

a high temp., after which, by a further rise of temp., the halogen compds. of higher mol. wt. first formed are decompd. to the metal or metalloid and the original halide. Examples are given of the prepn. of Mg, Na, Si and B.

29. C.A. 28, 6670^3 (1934) "Production of High-Melting Metals by Thermal Dissociation of Their Compounds" A. E. van Arkel. Metallwirtschaft 13, 511-14 (1934).

Metals such as Zr, Ti, Hf and Th, produced by the method previously described (C.A. 28, 5011^5) are more ductile than those made by melting, because they are free from impurities, especially O. As soon as these metals are exposed to air, a thin oxide layer forms on them. Zr and Ti prepd. by the iodide process can be rolled into rods and sheets. W is deposited in fairly large crystals, each of which is ductile, but their cohesion is very poor. By forming a W wire slowly it can be made from a single crystal, which is then ductile. Other metals, such as Mo and Zr, can be deposited on a W single crystal and they continue to form the same single crystal. Ductile V and Cr have also been obtained, but B and Si are always brittle and should not be considered metals. When B and Si are made, they are deposited on W wires: B diffuses into the W during the process. TiN and ZrN can be made by heating a wire in a mixt. of H, N and $TiCl_4$ or $ZrCl_4$. The nitrides have the same crystal structure as NaCl and are very brittle, but their elec. resistance is smaller than that of the corresponding metals.

30. C.A. 31, 1674^9 (1937) "Crystalline Boron" D. P. Mellor, S. B. Cohen and E. B. Underwood. Australian Chem. Inst. J. & Proc. 3, 329-33 (1936).

Cryst. B, prepd. by reduction of BBr_3 with H_2 at a hot W filament, has d. 2.36 and hardness about that of SiC. Spacings of 22 x-ray powder lines are given; attempts to find the unit cell were unsuccessful. Amorphous B prepd. by Moissan's method gives many powder lines coinciding with those of cryst. B, besides some diffuse bands.

31. C.A. 36, 2493^7 (1942) "Preparation and Properties of Boron" Howard E. Kremers. School Sci. Math. 42, 221-4 (1942).

Descriptive.

32. C.A. 38, 33^8 (1944) "Boron. I. Preparation and Properties of Pure Crystalline Boron" A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard. J. Am. Chem. Soc. 65, 1924-31 (1943).

The factors affecting the prepn. of B by the filament method and the types of products obtained are discussed. Single crystals of B of high purity and appreciable size were grown. Large single crystals were found in the form of needles or hexagonal plates. Smaller crystals were observed as hexagonal rods or massive in form. Optical evidence indicates that both the needle and plate forms of cryst. B may belong to the monoclinic system. Cryst. B shows great resistance to attack by various chem. reagents including O and oxidizing agents. This is in contrast to the great reactivity shown by finely divided B. Cryst. B shows the extreme hardness, great opacity, metallic luster, and elec. properties usually associated with semi-metallic solids. Change of elec. resistance with temp. is much smaller than has been previously reported; between 20 and 600° the increase in cond. is less than 100-fold. An x-ray powder diffraction pattern suitable for the identification of cryst. B was obtained. X-ray diffraction patterns of the needle crystals indicate a spacing of 5.06 A. along the needle axis, with two equal and orthogonal axes 8.93 A. in length lying in a plane perpendicular to the needle axis. The needle crystals were invariably found to be interpenetration twins, the components twinning along (130) with the needle axis in common. The unusual amount of symmetry shown by the needle crystals indicates that the natural system of this form of cryst. B may be tetragonal under ideal conditions of crystal growth. The smallest cell based on orthogonal axes found for the plate crystals has a = 17.86, b = 8,93, c = 10.13 A. No case of twinning was observed for these crystals. Probably the structures of the two cryst. forms are not fundamentally different.

33. C.A. 40, 3991^9 (1946) "Study of Boron" Jean Cueilleron. Ann. chim. 19, 459-86 (1944).

The prepn. of cryst. B of great purity was studied. Hackspill and Stieber's method (C.A. 26, 663), which consists in subjecting a mixt. of H and BCl_3 vapors to high-frequency elec. discharges, was carried out with BF_3, BCl_3, and BBr_3. The prepn. of the starting materials, amorphous B and B halides, is described. Amorphous B was obtained by Moissan's method (Compt. rend. 114, 392 (1892)), of reducing B_2O_3 with Mg. In order to avoid Si impurities an iron crucible was used instead of a clay crucible. The reaction product was finely ground and treated with boiling HCl until a brown homogeneous suspension formed. The boiling suspension was filtered on a Buchner funnel with fritted disk and the B washed on the filter with boiling H_2O, to remove almost all H_3BO_3 in one operation. The B was then purified as described by Moissan. BCl_3 and BBr_3 were synthesized from amorphous B and Cl or Br, resp. (cf. Moissan, Ann. chim. 6, 296, 312 (1895)) in special app., and purified by known methods. BF_3 was obtained from B_2O_3, CaF_2, and H_2SO_4 (cf. Davy, Phil. Trans. 102, 365 (1812)). Since no Pt vessels were available, the reaction was carried out in iron and Pyrex equipment; this led to considerable SiF_4 impurities. Amorphous B crystallizes by fusion in an atomic hydrogen blowpipe and shows the x-ray spectrum of crystd. B. The properties of B and its halides are reviewed, and some new properties are established. A mixt. of B with $KMnO_4$, Pb, or Sb oxides or $Pb(NO_3)_2$ ignites on shock or friction without detonation. B explodes with HI. A mixt. of B and Sb_2O_3 ignites upon heating. Solns. of BCl_3 or BBr_3 in Br are nonconductors. The b.p. of BBr_3 was detd. as 91.3°. BBr_3 explodes with ether and alc. It reacts in the cold with SO_3. A violent reaction takes place with H_2SO_4 and oleum. With S_2Cl_2 a gas, S_2Br_2, b. 10-12°, is developed. A soln. of BBr_3 in triethanolamine heated with Mg to 120° for 3 hrs. in a sealed tube does not form any addn. compd. K explodes with boiling BBr_3, while Na does not react at all. In a cryoscopic study of the system B-BBr_3 a eutectic was found at a compn. of 80% BBr_3-20% B, m. 60.4°. The reduction of BCl_3 and BBr_3 with H, in an electric arc, with W electrodes was studied. According to the diam. and the temp. of the electrodes, crystd. B deposits on the electrodes, or a very fine powder of B which, with H_2O, forms a colloidal suspension, collects on the walls of the flask. By working with electrodes 6 mm. in diam. at low temps., B powder is obtained almost exclusively. For BBr_3, the yield is 30%. However, with the same electrodes heated to incandescence, only crystd. B forms. The use of electrodes of small diam. (0.7 mm.) heated to redness also causes the formation of only crystd. B, while with 1.5-2.0 mm. electrodes heated nearly to redness both varieties are formed. B prepd. by this reduction from BCl_3 or BBr_3 contains practically no Si. Different results are obtained when

BF_3 is reduced in an elec. arc. Only small quantities of crystd. B, contg. Si impurities, are formed. Colloidal suspensions are stable for several months. At a concn. of 2-3 g. per l., the suspension is dark brown and opaque; at lower concns. it is yellow and transparent. The sol gives the Tyndall effect, but no fluorescence. It is slightly acid (pH 6) owing to the presence of some H_3BO_3, HBr, or HCl. The colloid soln. cannot be flocculated by heating or freezing; however, it can be pptd. with electrolytes. In HCl, H_2SO_4, or HNO_3 medium, flocculation occurs at pH 2, in alk. medium at pH 10. The sol is rather stable in the presence of NH_3, but it is pptd. with EtOH, acetone, CCl_4, $CHCl_3$ or ether. After evapn. of the soln. in vacuo at ordinary temp., the residue peptizes again, if it has not been desiccated too far. Ultracentrifuging at 100,000 r.p.m. causes a light deposit, which increases with time. However, after 1 hr., the remaining soln. is still colloidal. Colloidally dispersed B reacts, in the cold, with HNO_3, H_2O_2, $KMnO_4$, and $AgNO_3$. It does not react with nascent H, HF, or boiling HI. The m.p. of B has been detd. by different authors as between 2000 and 2500°. C. detd. the m.p. in the atomic hydrogen blowpipe as 2075°.

34. C.A. 40, 4579^3 (1946) "Preparation of Pure Crystalline Boron and the Measurement of Its Hardness" Marcel Formstecher and Eugene Ryskevic. Compt. rend. 221, 747-9 (1945).

Pure cryst. B is formed by passing a mixt. of H and BH_3 over a filament of W or Mo at temps. of 1250 to 1400° in a quartz tube. The Mo or W is removed chemically. Two samples gave an analysis of 99.2% B. The d. of the B is given as 2.34 = 0.01 at 20° and the hardness as 5000 kg./sq. mm.

35. C.A. 40, 7112^7 (1946) "The Amorphous Structure of Metalloids, Metals, and Alloys". Hans Richter Physik. Z. 44, 406-41 (1943).

Thin noncryst. films of B, Ga, Si, As, P, S, In, Sn, Tl, Sb, Se, Pb, Te, Bi, and I, formed by vaporization, melting, or pptn. were studied by means of electron transmission and reflection. The existence of an amorphous phase is demonstrated. The spacing of the rings in the diffraction pattern in transmission differs from that obtained by reflection. This spacing is the same as is observed with x-rays and liquid metal. Thin films of the following alloy systems were investigated: As-Sb, Sb-Se, Ga-Sb, Ga-In, Sn-Bi (eutectic), Sn-Pb (eutectic), Pb-Bi (eutectic), Sn-Bi-Pb (rose metal), and Sn-Bi-Pb-Cd (Lipowitz metal). They likewise have an amorphous phase. 106 references.

36. C.A. 41, 4050b (1947) "Amorphous Boron". Worth C. Goss. U.S. 2,415,946, Feb. 18, 1947.

Na tetraborate, NaCl, and powd. charcoal are used in a three-step process to produce amorphous B suitable for use in explosives, NaOH and HCl being salable by-products. The reaction takes place according to the following steps: I. $2NaCl + 2H_2O = 2NaOH + H_2\uparrow + Cl_2\uparrow$; II. $Na_2B_4O_7 + 7Cl_2 + 7C = 4BCl_3\uparrow + 7CO\uparrow + 2NaCl$. III. $2BCl_3 + 3H_2 = 6HCl + 2B$. Step I is the electrolysis of the salt, the Cl being used in step II which is carried out in an elec. furnace. Anhyd. borax is mixed with powd. charcoal and the mix is melted and fed to the furnace in a molten state. Gaseous Cl_2 is introduced into the bottom of the furnace. Gaseous BCl_3 passes out of the furnace and is condensed. The third step is the reduction of BCl_3 with the H_2 produced in I. A rotary elec. furnace is used for III, with B dust being suspended in the furnace atm. to catalyze the reaction.

37. C.A. 43, 4593g (1949) "Preparing Boron of High Purity". Roland Kiessling. Acta Chem. Scand. 2, 707-12 (1948).

An app. and the procedure for prepn. of B by the reduction of BBr_3 vapor with H are described, and the yields obtained at different temps. and for different reaction times are given. At 800°, 1-2 g. B can be obtained in 14 hrs. The B has a mean purity of 98.9%, contg. 0.4% Al and 0.1% Si as impurities.

38. C.A. 43, 5162e (1949) "Elemental Boron". Frank J. Sowa. U.S. 2,465,989, April 5, 1949.

Elemental B was produced economically in 50 to 90% purity by fusing a fluoborate intimately mixed with an alkali or alk. earth metal. One mol. of Na was cut in pieces 5 mm. and finer, and mixed with 0.33 mol. KBF_4. The mixt. was fused in an Fe tube under a 1 in. layer of NaCl at 250 to 550°. After cooling the fused product was ground to 50 mesh, digested in boiling H_2O, then in boiling 25% HCl, and the residue contg. 84% elemental B was filtered off and dried. KF and NaF were recovered as by-products. Alternatively, 4 mols. Na were dissolved in 500 ml. of liquid NH_3 in a stainless steel beaker and 1 mol. KBF_4 was mixed in the soln. When the NH_3 evapd. the mix was covered with a layer of NaCl and fused. The product was crushed and washed as before, and then extd. with 2200 g. of molten NH_4HF_2 in order to remove nitrides. A fluoborate of 95% or higher purity is recommended, since Si or Al compds. will appear in the B product if present. Suitable dispersions of the metal and the fluoborate may be produced by milling them together or by extruding the metal into wires or by stirring the salt into a low-melting alloy, such as Na-K alloy.

39. C.A. 43, 6133i (1949) "X-Ray Powder Patterns of Boron-Coated Molybdenum and Tungsten Filaments". St. v. Naray Szabo and Charles W. Tobias. J. Am. Chem. Soc. 71, 1882-3 (1949).

Pure B was prepd. by the thermal decompn. of BBr_3 in an app. which was a modification of Van Arkel's method. The BBr_3 was prepd. by Mayer and Zappner's modified Moissan method. B was deposited in a dense cylindrical layer on Mo and W filaments suspended between Pt electrodes during the coarse of the thermal decompn. of BBr_3 in the app. On both W and Mo 2 types of deposits were noted: at 1000-1300° graphitic, grayish, and amorphous, at 1500-1600°, dark green cryst. surfaces. The diam. of the B coated onto the W and Mo filaments was 400-500 μ, while the core diam. was 50-100 μ; the sp. gr. av. was 2.33. All the B collected on the W and Mo filaments was investigated with a 5 cm. radius cylindrical camera with Cu-K α-rays. The x-ray patterns of W and Mo were easily singled out; the 2 types of deposits, i.e. the graphitic and cryst., gave different patterns, but the same type of deposit on the 2 filament materials gave identical patterns, indicating that there was no alloy formation between B and the filament material. The reflections of the graphitic-type B coating could be indexed using a tetragonal elementary cell (a = 8.57 A., c = 8.13, 78 atoms/cell). The cryst. deposit had a pattern suggesting a hexagonal cell (a = 11.98 A., c = 9.54 A., 180 atoms/cell).

40. C.A. 45, 3265g (1951) "Resistor Furnace for the Production of High-Purity Boron". Guy H. Fetterley U.S. 2,542,916, Feb. 20, 1951.

The resistor rods (2 in. in diam.) are of graphite and are supported from the threaded studlike part of the lead-in conductor by a massive cylindrical block of high-grade graphite. Deposition of solid reaction products on the supporting block is prevented by the large surface of contact with the circulating gases and also by internal cooling effected by circulating water through the chamber in the metallic stud portion of the graphite block. Operating temps. are maintained at 1400° while the temp. of the graphite block is kept at about 700° or less.

41. C.A. 45, 5601g (1951) "Reduction of Refractory Oxides" Thayer Lindsley and Peter P. Alexander. U.S. 2,545,821, Mar. 20, 1951.
    Refractory oxides are reduced by heating the oxide in vacuo to 800-900° with LiH (I), and leaching out the resulting Li_2O with H_2O. Suitable refractory oxides are those of Cr, Be, B, Zr, U, and Ta. Alloys may be prepd. by mixing a metal, such as Ni or Co, with an oxide and I.

42. C.A. 46, 45b (1952) "Electrolytic Production of Boron" Hugh S. Cooper U.S. 2,572,248, Oct. 23, 1951.
    Pure B is deposited on the Cu cathode of an electrolytic cell contg. KCl and KBF_4 in a graphite crucible protected by an outer shell of Inconel and operating at 800-850°. In U.S. 2,572,249, B_2O_3 is added to the KCl and KBF_4 electrolyte, as used in above abstr., and the black scum formed during electrolysis is removed to make B C-free. The cell has an Fe cathode; in an example given the current was 2500-4000 amp. at 7-10 v.

43. C.A. 46, 10,978g (1952) "Electrolytic Production of Boron". Walter M. Weil. Brit. 677,392, Aug. 13, 1952.
    See U.S. 2,572,248-9 (C.A. 46, 45b).

44. C.A. 46, 11,087d (1952) "Production of Metals From Their Halide Compounds". Donau Chemie A.-G. Austrian 169,067, Oct. 10, 1951.
    The metal chlorides (especially of Ni, Cr, B, Al, Si, Ti, V, Mn, and Be) are treated with NH_3 or org. bases. The additive compds. obtained are mixed with amalgams of reactive metals, e.g. Na. The amalgam may be obtained in the reduction process itself, e.g., by adding Hg during the electrolysis of a molten mixt. of alkali halides and $AlCl_3$. The amalgam formed reacts with the residual $AlCl_3$ to give Al. The method is especially useful for obtaining metals (except noble metals) in pure form to be used as catalysts.

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Report No. T9.35.0-1-1

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THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

STABILITY OF CONSTRUCTION MATERIALS TO THE DIMETHYL ETHER - BORON TRIFLUORIDE COMPLEX. Progress Report No. 1.

March 30, 1953

Work by:

Gene Elder
Henry Nevers

Report by:

Henry Nevers

Sentence Summary

Preliminary studies were made of the action of the dimethyl ether-boron trifluoride complex and its decomposition product on aluminum, SAE 40 brass, and ceramic column packing.

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DECLASSIFIED

I. INTRODUCTION:

In connection with Contract No. AT(30-1)-1506 (Job No. 32-4111) for the Atomic Energy Commission it is necessary to obtain information on the affect of the dimethyl ether-boron trifluoride complex (polymer) on various materials of construction. This report describes some rapid tests which were made on aluminum, brass, and ceramic column packing.

II. SUMMARY OF PREVIOUS WORK:

In Volume 5, Division III of the National Nuclear Energy Series, Manhattan Project Technical Section, extensive corrosion tests on monel and other metals are described. Metals were generally little affected by dry polymer, while wet polymer was much more corrosive.

III. SUMMARY AND CONCLUSIONS:

In tests of 1 to 4 days duration, SAE 40 Brass samples, white porcelain saddles and "Intalox" stoneware saddles for packing distillation columns were not significantly affected by either dry or wet boiling polymer (118-127°C.). An aluminum rod suspended in a condenser above a large mass of decomposing and boiling polymer did not deteriorate noticeably in 11 days.

IV. RECOMMENDATIONS:

The tests reported here were relatively short and could probably give only indications of extreme corrosiveness of the media upon the specimens tested. A better estimate of the effect of polymer and decomposition gas on materials of construction should be obtained by tests of much greater duration.

V. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL RESULTS:

Notebook References: Laboratory Book Nos. 330, pp. 39-41; 331, p. 4.
Assignment No. A-407.

The tests of the ceramic packing and SAE 40 brass were run by immersing the samples in from 200 to 300 ml. of polymer in a 1 liter flask having a thermowell extending nearly to the bottom of the flask into the liquid. It was necessary to break the ceramic saddles from their nominal 1 inch size into pieces which could be introduced into the 24/40 standard taper necks of these flasks. The SAE 40 red brass samples were rectangular pieces 1 inch long by 1/2 inch wide and 1/32 inch, 1/16 inch, or 1/8 inch in thickness cut from 1/2 inch thick plate. In each test of the brass pieces of all three thicknesses were used. The boiling flask was surmounted with a water-cooled Friedrich condenser open to the atmosphere. Heat was provided to the flask by the bottom half of a Glas-Col heating mantle. (Fig. 1). In most of these tests polymer as prepared was used with the additions of 2% water to make the test as rigorous as possible. In one or two of the tests polymer which had been "degassed" was used; that is the polymer was boiled under 7-12 cm. Hg. pressure for an hour or more to remove dissolved gases. After the test the samples were washed free of polymer, then dried at 110°C. and reweighed. A visual comparison of the tested samples was made with some of the untested material. The complete data are in Table I, while a diagram of the apparatus used is in Figure 1.

The test of the aluminum was made by suspending a cylindrical aluminum rod 45 cm. long and .5 cm. in diameter in the glass condenser of a one gallon polymer distillation unit for 11 days, the weight before and after the test being obtained, and a visual comparison made with a similar untested aluminum rod. The results of this test are given in Table I.

VI. DISCUSSION:

The first test, with "Intalox" saddles, was made with degassed polymer. The other tests were made with polymer which had not been degassed, and the presence of excess BF_3 would be expected to make the material even more corrosive than pure polymer. The tests with wet, undegassed polymer were presumably the most severe.

The white crystalline deposit found on the ceramic saddles was soluble in water, though insoluble in acetone. The material may have been boric acid, since even the dry polymer was in contact with wet air during the refluxing. The weight loss shown by one of the brass samples may not be significant, since another sample showed no weight loss when boiled with wet polymer.

The temperature drop during the runs was presumably due to the accumulation of liquid decomposition products in the distillation flask. The principal product is presumably the methyl borate-boron trifluoride complex. The polymer became dark brown by the end of each run; a similar behavior is observed in glass equipment in the absence of added solids.

REPORT BY: Henry [illegible] DATE: March 24, 1953

READ AND UNDERSTOOD BY: Kenton Atwood DATE: March 30, 1953

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FIGURE 1.

Reflux Apparatus.

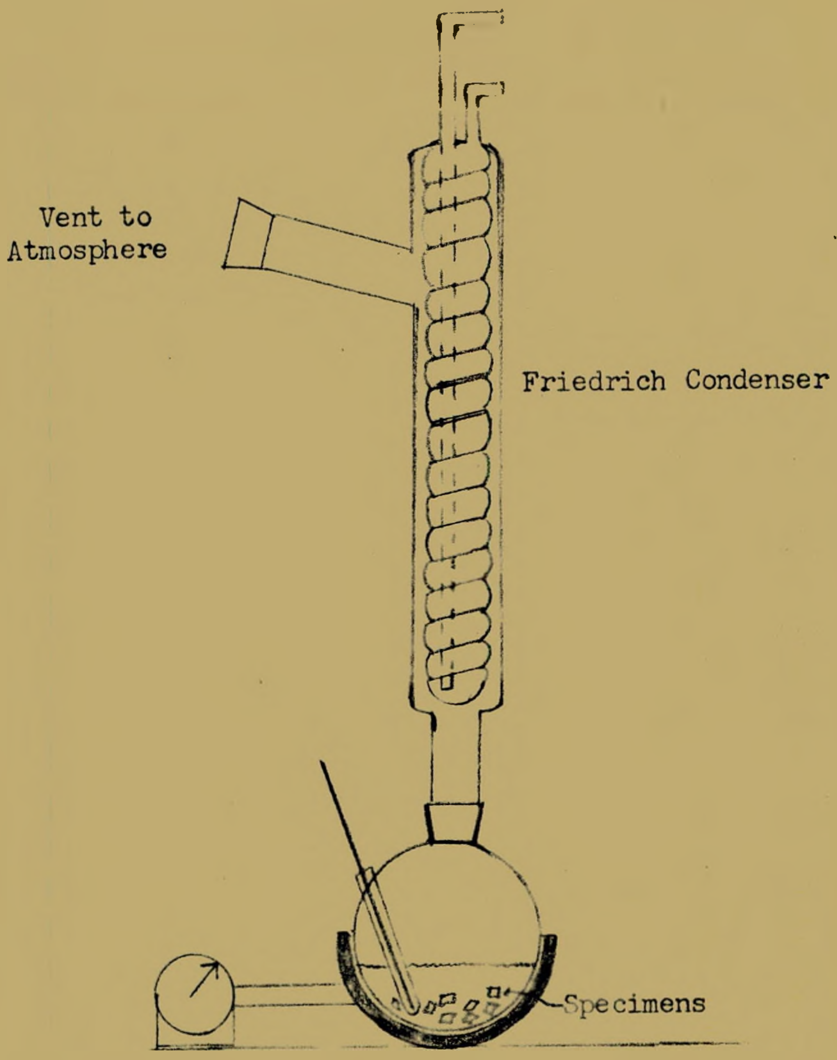

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TABLE I.

CORROSION TEST OF SP[illegible]NS IN POLYMER AND IN DECOMPOSITION GAS.

	Specimen Type and Source	Description Specimen	Pretreatment Specimen	Wt. Sample (g.)	Polymer Description	Total Reflux Time (days)	Initial Temp. Polymer °C.	Final Temp. Polymer °C.	Final Treatment	Final Wt. (g.)	% Wt. Loss	Remarks
1.	"Intalox" Saddles U.S. Stoneware Co. Ravenna, Ohio	Brown-gray ceramic saddles 1" size	Dry 160-170°C. 1 hour	74.8 g.	Degass[illegible]	1.0	127	123-124	Soak acetone 2 hrs. Dry 160°C., 1 hr.	75.0	gain	Strength unchanged. Brown deposition on saddles when dried with acetone.
2.	"Intalox" Saddles U.S. Stoneware Co. Ravenna, Ohio	Brown-gray ceramic saddles 1" size	Soak acetone 1 hour. Dry 160-170°C., 1 hour.	101.3	Not de[illegible]sed	2.0	126	120	Soak acetone overnight. Dry 110°C., 1 hr.	102.0	gain	Strength unchanged. Brown deposition on saddles when dried with acetone. Also white crystalline deposit on saddles.
3.	"Intalox" Saddles U.S. Stoneware Co. Ravenna, Ohio	Brown-gray ceramic saddles 1" size	none	81.5	Not de[illegible]sed 2.[illegible] H_2[illegible] [illegible]ed	3.0	126	118	Soak acetone overnight. Dry 110°C., 1 hr.	82.2	gain	Strength unchanged. Brown deposition on saddles when dried with acetone. White crystalline deposit on saddles.
4.	White porcelain Saddles U.S. Stoneware Co.	White ceramic saddles 1" size	none	74.0	Not [illegible] 2[illegible] H_2[illegible]	1.[illegible]	126	122	Soak acetone 1 hr. Dry 110°C., 1 hr.	74.0	none	Saddles darkened to gray. No change in strength.
5.	SAE 40 Brass American Brass and Aluminum Co. Louisville, Ky.	Light copper color, pieces 1"x1/2"x1/32" 1"x1/2"x1/16" 1"x1/2"x1/8"	Dipped conc. HCl 30 sec., washed acetone Dried 110°C. 15 min.	37.0	Poly[illegible]t dega[illegible]	4.0	127	119°C.	Soak acetone overnight Dry 110°C., 1 hr.	36.0	1.0	Dull blotches on surface. No visual evidence of corrosion Note weight loss.
6.	SAE 40 Brass American Brass and Aluminum Co. Louisville, Ky.	Light copper color, pieces 1"x1/2"x1/32" 1"x1/2"x1/16" 1"x1/2"x1/8"	Dipped conc. HCl 30 sec. washed acetone Dried 110°C. 15 min.	63.5	Not [illegible]d 2[illegible] H_2[illegible]d	1.[illegible]	127	122	Soak acetone 1 hr., Dry 110°C., 1 hr.	63.5	none	No visual evidence of corrosion No weight loss.
7.	Aluminum	Aluminum Rod from aluminum welding rod 45 cm. long x .5 cm. diar.	none	20.9	No pol[illegible] used. [illegible]sus-[illegible] con-[illegible] [illegible]one [illegible] [illegible]lla-[illegible] [illegible] [illegible]com-posit[illegible].	11	---	---	none	21.5	gain	Surface dulled, like film of aluminum oxide, no loss of strength indicated.

* "Degassed" polymer is that which has been boiled under 7-12 cm. Hg. [illegible] vacuum for an hour or more (70-[illegible]0°C.)

The polymer was dark brown after completion of each run.

867-LLA

Report No. T1.25-4-1

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THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

DEHYDRATION OF DIMETHYL ETHER. Progress Report No. 1.

March 30, 1953

Work by:

Robert Habermehl
W. M. Keely

Report by:

Robert Habermehl

Sentence Summary

This report deals with the method for analyzing dimethyl ether for water vapor, and the removal of water vapor from dimethyl ether by the use of various desiccants, such as activated alumina.

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DECLASSIFIED

I. INTRODUCTION:

As part of the work for the Atomic Energy Commission under Contract No. AT(30-1)-1506 (Job No. 32-4111) a study of methods for drying dimethyl ether was undertaken. The object of the work was to develop a practical commercial method for removing the small amounts of water, of the order of 0.1%, which are present in tank dimethyl ether.

II. SUMMARY:

It was found that all the desiccants studied absorb a portion of the dimethyl ether passing over them. Preliminary results indicate that the ether materially affects the ability of activated alumina to absorb water. The alumina may be reactivated, but it is indicated that complete reactivation may be difficult. An analytical method which can be used in determining water concentrations as low as 0.01% is described.

III. CONCLUSIONS:

The preliminary results indicate that alumina will remove essentially all water from dimethyl ether containing from 0.02 to 0.55 wt. % water, at a space velocity of 400 at room temperature. Alumina will initially take up from 1 to 3% of its dry weight of water before water "breaks through", even at the low water concentration. After regeneration the drying efficiency of the alumina is reduced, at least for ether containing 0.55% water. All of the desiccants studied absorb considerable amounts of dimethyl ether.

IV. RECOMMENDATIONS:

It is recommended that further work be done on the use of alumina as a drying agent for $(CH_3)_2O$ both before and after regeneration. More work should be done on the method for determining water vapor and if possible the sensitivity should be increased. A better water saturator should be devised if studies with higher concentrations of water vapor are to be continued.

V. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL DATA:

Reference: Laboratory Book 312, pp. 98-138. Assignment No. A-407.

A. Experimental Results.

Drying bulbs containing anhydrone and P_2O_5 were arranged in series and $(CH_3)_2O$ passed through them. The bulbs were weighed before and after passage of the ether and their weight increase recorded. These data are recorded in Table I. The increase in weight of Bulb 2 should indicate dimethyl ether absorption alone. The same anhydrone was used in Bulb 2 in Runs 1 and 2, and the same P_2O_5 was used in Bulb 1 in Runs 1 and 3.

TABLE I.

Absorption* of $(CH_3)_2O$ on Anhydrone and P_2O_5

Run No.	Vol. $(CH_3)_2O$ liters	Bulb 1 Reagent	Bulb 1 Wt. Increase gms.	Bulb 2 Reagent	Bulb 2 Wt. Increase gms.
1	30	P_2O_5	0.0631	Anhydrone	4.0423
2	20	Anhydrone	3.9331	Anhydrone	1.4651
3	20	P_2O_5	0.0738	P_2O_5	0.0487

Dimethyl ether was then passed through a series arrangement of drying bulbs containing alumina and silica gel. This test was conducted for increasing intervals of time and volume of ether passed to check possible saturation of the reagents. The same charges of desiccant were used for all the runs. These data are recorded in Table II. The column "% ether absorbed" refers to the percentage of the additional weight of ether passed during this time interval and not to the total weight of ether from previous passes.

TABLE II.

Sorption of $(CH_3)_2O$ on Alumina and Silica Gel.

Run No.	Vol. $(CH_3)_2O$ passed per interval of run	Total Vol. $(CH_3)_2O$ passed	Bulb 1 (Alumina) Wt. Increase	Bulb 1 (Alumina) % Ether Absorbed	Bulb 2 (Alumina) Wt. Inc.	Bulb 2 (Alumina) % Ether Absorbed	Bulb 3 (Silica gel) Wt. Inc.	Bulb 3 (Silica gel) % Ether Absorbed
1	30	30	1.5549	2.5	2.0006	3.26	3.7485	6.1
2	30	60	0.0588	0.096	0.0191	0.031	-.003	-
3	30	90	0.0445	0.073	0.0057	0.009	-.0374	-
4	30	120	0.0390	0.064	0.0328	0.053	.0067	0.011
5	30	150	0.0543	0.088	0.0836	0.136	.0091	0.015
6	60	210	0.0050	0.004	0.0591	0.048	-.0879	-
7	60	270	0.0618	0.050	0.0961	0.076	0.0584	0.048
Total Approx. Wt.	-	270	1.8183	0.32	2.2969	0.42	3.6940	0.67

The bulbs used contained approximately 30 g. of each reagent. From Table I, the increase in weight of Bulb 2 indicates that anhydrone absorbed ether equivalent to 13% of its dry weight in Run 1, and an additional 4.9% in Run 2. P_2O_5 absorbed ether equivalent to 1.6% of its dry weight in Run 3.

From Table II, the total increase in weight of Bulb 2 indicated that alumina absorbed ether equivalent to 7.7% of its dry weight. The total increase in weight of Bulb 2 indicates that silica gel absorbed ether equivalent to 12.3% of its dry weight, Bulb 1 is not considered in either case because a portion of its weight increase is due to water vapor. The alumina and silica gel were continuing to absorb ether at the end of 4-1/2 hrs. or 270 liters of $(CH_3)_2O$. However, both apparently absorb less than 1% of the ether being dried.

Dimethyl ether from Cylinder M1515, The Ohio Chemical and Manufacturing Co., was passed over a 25 cc. bed of Alcoa Type F-1 activated alumina (as received, +4 to -8 mesh) at a space velocity of 400. The inlet and outlet streams of ether were analyzed for water content; data are recorded in Table III. The term space velocity indicates volumes of ether, measured at room conditions passed per volume of catalyst per hour.

TABLE III.

The Removal of Water Vapor From $(CH_3)_2O$ by Alcoa F-1 Alumina.

Vol. $(CH_3)_2O$ Passed Over Alumina, Liters	% (wt.) Water Inlet	% (Wt.) Water Outlet	% Water (dry weight) on Alumina
0	0.022	-	-
0	0.018	-	-
23.3	-	0.018	-
60	-	0.0096	-
257	-	0.00	0.58*
287	-	0.00	0.64*
497	0.018	0.004**	1.1*
538	-	0.005**	1.2*
980	0.011	0.005**	2.2*
1730	0.021	0.016	-

* These figures assure 100% efficiency of absorption and an inlet concentration of 0.02%. The first two values are assumed in error.
** Required only 0.6 to 0.8 cc. titration and may be within limits of experimental error.

In order to obtain more rapid and reliable measurements it was decided to make runs with ether saturated with water vapor. Apparatus for the saturation is shown in Figure 1. The ether was metered into a water saturator held at a constant temperature by a water bath and analyzed for water content before and after passage over alumina. Erratic results were obtained on the water content of the saturated ether, but the concentration finally lined out to an average value of 0.55% H_2O by weight. This saturated ether was then passed over 25 cc. of F-1 activated alumina that had received additional activation in the laboratory by being contacted with a N_2 stream overnight at 350°F. The results are listed in Table IV.

TABLE IV.

The Removal of High Concentrations of Water Vapor From Activated Alcoa F-1 Alumina.

Inlet gas = 0.55% H_2O - Space Velocity = 400

Vol. $(CH_3)_2O$ Passed	% H_2O (wt.) Outlet	% H_2O (dry weight) on Alumina
14.1	0.00	0.86
25.5	0.00	1.56
37.8	0.0096	2.3
45.5	0.0102	2.8

The alumina was reactivated overnight with a stream of N_2 in a furnace at 350°F., and again tested (Table V).

TABLE V.

Effect of Reactivation at 350°F. on Removal of Water Vapor From Ether by Alumina.

Inlet Gas = 0.55% H_2O Space Velocity = 400

Vol. $(CH_3)_2O$ Passed	% H_2O (wt.) Outlet	% H_2O (dry weight) on Alumina
10.3	0.034	(No calculations made since results did not indicate complete absorption)
19.9	0.014	
35.4	0.014	
45.2	0.011	
145.5	0.14	

In another study, the alumina used to remove 0.02% H_2O from ether (Table III) was reactivated overnight in a stream of N_2 at 500°F. and tested with ether containing 0.55% H_2O (Table VI).

TABLE VI.

Effect of Reactivation at 500°F. on Removal of Water Vapor From Ether by Alumina.

Inlet Gas = 0.55% H_2O Space Velocity = 400

Vol. $(CH_3)_2O$ Passed	% H_2O (wt.) Outlet	% H_2O (dry weight) on Alumina
6.8	0.0068	0.4
34.8	0.017	2.0
162.	0.50	-

B. Analytical Method for Water in Dimethyl Ether.

Karl Fischer reagent was used to titrate the water in the ether; the water was collected using an adaptation of the method and apparatus employed by Mitchell and Smith (1) for condensible gases. However in place of their apparatus, a "Bird" shape flask patterned after the Shaw sulfur flask was used and evaporation of the ether was accomplished by slowly warming it to room temperature instead of using a vacuum pump. The method may be followed by referring to Figure 1.

25 cc. of absolute methanol are placed in the "Bird Flask", the flask is stoppered, stopcocks A and B closed and the flask is shaken to absorb any water on the sides of the flask. The glass stopper is then removed and the methanol titrated with Karl Fischer reagent to an endpoint that persists when the flask is stoppered and shaken. 10 cc. of methanol are pipetted into this "pretitrated" methanol and this additional methanol is titrated to the endpoint. This serves as a blank for the determination. For the actual analyses, the final 10 cc. are not titrated. When the flask is prepared containing 25 cc. of "pretitrated" CH_3OH and 10 cc. of untitrated CH_3OH, it is placed in the system for water analyses by connecting the arm that extends to the bottom of the flask to the sample point of the ether stream through stopcock B. Both stopcocks are opened and the flask is slowly lowered into a dry ice-acetone bath. Stopcock B is opened to prevent pulling a vacuum on the saturation system when the flask is cooled and the drying tube prevents pulling in water vapor from the atmosphere. When the flask is lowered into the condensing bath, the dry gas meter is read and recorded. After a sufficient sample has condensed in the flask, (usually 25 l.) stopcock A is closed and the flask disconnected from the sample point. The flask is then removed and the ether is slowly vaporized through the drying tube until most of it has disappeared as evidenced by the return to approximately the original volume in the flask. The flask is then removed from the manometer-drying tube system. To remove any water trapped in the arm of the flask extending to the bottom of the flask, open both stopcocks, stopper the flask and close stopcock B until the vapor pressure of residual ether forces the methanol solution to the top of the arm, then open B, close A and B, remove the stopper and titrate. This titration value minus the blank is due to the water in the ether stream. The calculation of water content is made as follows:

$$\% \ H_2O = \frac{(a-b) \times R \times (t+273)}{V \times P \times 7.58}$$

where

a = ml. of KF reagent for sample.
b = ml. of KF reagent for blank.
R = water equivalence of KF reagent in mg. H_2O/ml. KF reagent.
V = Volume of ether, liters measured.
P = Barometric pressure, mm. of Hg.
t = Room temperature, °C.

The constant in the equation would be 7.38 if the ideal gas laws were used; the actual constant includes a correction for gas imperfection..

VI. DISCUSSION:

Alcoa (2) recommends flow rates of 10 to 20 ft.^{3} per hour per lb. of catalyst for complete drying of commercial gases. This corresponds to 10 to 20 l./hr. for 25 cc. samples. Actually a flow rate of 10 l./hr. was used. At this flow rate, it requires 2 hrs. and 30 mins. to collect a 25 l. sample of ether in the "Bird" flask. This gives approximately a 50 g. sample of ether when corrected to standard conditions. In the titrations of the samples, Karl Fischer reagent was used having a water equivalence varying from 1 to 3 mg. H_2O/cc. It can be seen that for ether streams containing small amounts of water, the titrations will be small; i.e., for 0.02% H_2O and Karl Fischer reagent equivalence of 1 mg. H_2O/cc., 10 cc. of reagent will be required. The admission of 1 mg. of H_2O through faulty technique would therefore make an error of .002% in the ether. Therefore a value of 0.01% H_2O in the outlet from a drying tube, was chosen as indicating the "break through" of water.

VII. LITERATURE CITED:

1. Mitchell, John and Smith, Donald Milton, Aquametry, Interscience Publishers, Inc., New York, 1948.

2. Aluminum Company of America, Activated Alumina - Its Properties and Uses, Chemicals Division, Pittsburgh, Pennsylvania, 1949.

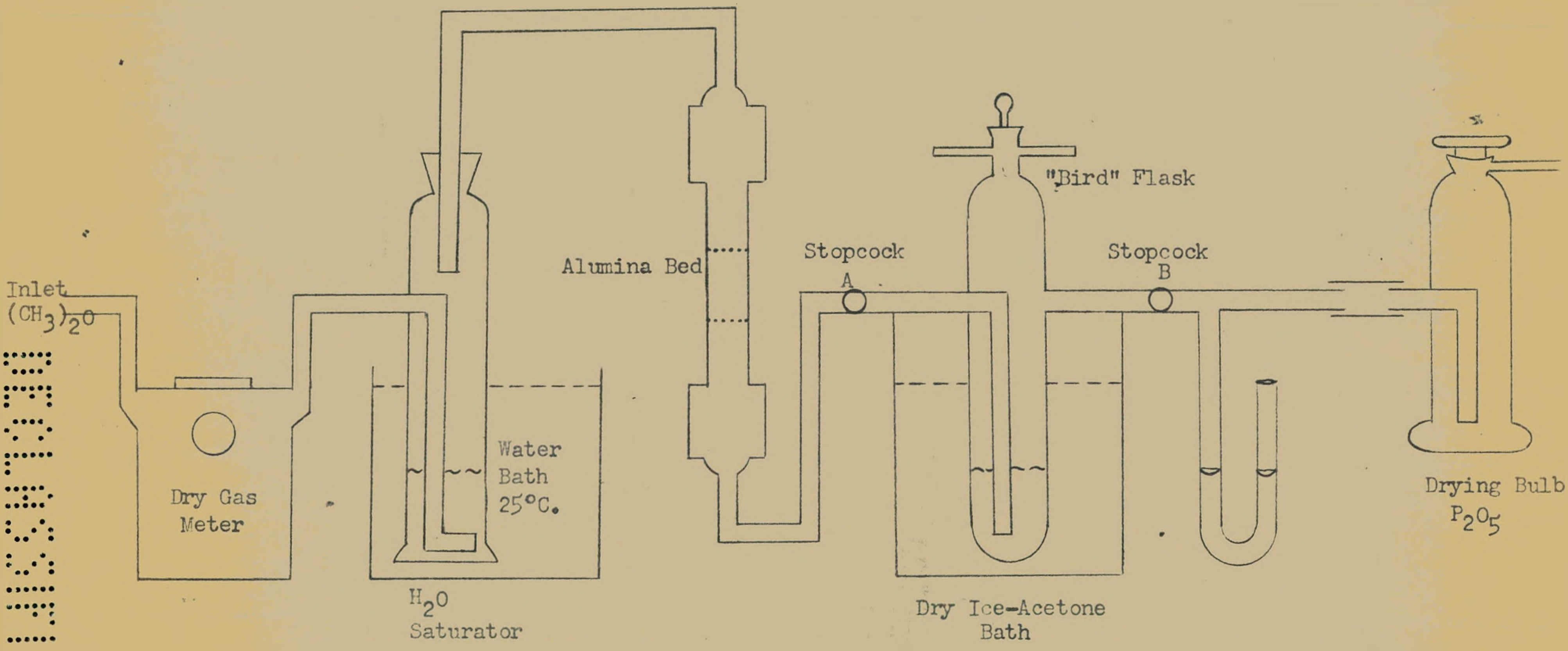
REPORT BY: DATE: 3-31-53

READ AND UNDERSTOOD BY: Kenton Atwood DATE: March 31, 1953

jc

FIGURE 1.

SATURATION AND TESTING APPARATUS.



Report No. T9.44-1-1

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THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

CHARACTERIZATION OF A TWO INCH DISTILLATION COLUMN PACKED WITH PROTRUDED METAL PACKING.

March 30, 1953

Work by:	Report by:
O. C. Bradley	O. C. Bradley
H. W. Fleming	Kenton Atwood

Sentence Summary

A two inch distillation column was characterized, using a n-heptane-methyl cyclohexane mixture.

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I. INTRODUCTION:

As part of the work under Contract No. AT(30-1)-1506 (Job No. 32-4111) for the Atomic Energy Commission, it was necessary to characterize a distillation column. The object of the work was to determine pressure drop across the column and the theoretical plates through use of the standard mixture of n-heptane-methyl cyclohexane generally used in this type of work.

II. SUMMARY AND CONCLUSIONS:

The behavior of the distillation column, which was 2 inches in diameter and was packed with 4.5 feet of 0.24" by 0.24" protruded #316 stainless steel packing, was found to be very similar to that which was predicted for this type of packing.

III. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL DATA:

Reference: Notebook No. 293, pp. 156-9; No. 331, pp. 1-3.
Assignment No. A-407.

A. Equipment.

1. Column.

A column was constructed of the design shown in Figure 1. A 5 ft. monel tube, 2" I.D. was arc welded to a set of 65/40 #304 stainless steel ball and socket joints. Initially a #309 stainless steel plate perforated with 5/32" holes was placed in the column as a packing support. However, this produced too much back pressure on the system and was replaced by a 6" cone made of 12 mesh stainless steel. This cone rests on the shoulder provided by the welding of the 65/40 male joint at the bottom of the column.

The packed portion of the column is 4-1/2 ft. high and has a cross sectional area of 0.02330 sq. ft. Packing was placed only within the heated portion of the column.

The column is heated by three 500 watt heaters as shown in Figure 1. A differential thermocouple and a thermocouple is located at the midpoint of each heater, i.e. 10", 30", and 50" from the bottom of the column.

2. Distillation Pot.

Figure 2 illustrates the metal distillation pot. It is constructed of a 6" I.D. Monel tube with a #310 stainless steel plate arc welded on each end. The top has a #304 stainless steel female 65/40 joint arc welded to fit the bottom of the column. Two 1/4" #304 stainless steel nipples are welded near the top at a 45° angle for gas or liquid introduction. A 1/4" thermowell (#310 S.S.) extends inside from the top to 1/4" from the bottom of the pot.

The sampling connection at the bottom is constructed from a 1/4" #304 stainless steel nipple with a series of concentric stainless tubes welded inside to reduce the inside diameter to 1/16" I.D., a 1/4" needle valve (#304 S.S.) is threaded on the nipple then a 1/16" I.D. stainless steel tube welded on the outlet of the valve. This setup facilitates taking a sample with a minimum hold-up in the connection.

A sight glass is arranged with an outlet for determining the back pressure as shown in Figure 2.

Heating the pot is accomplished by two 1000 watt heaters, the lower one being extended over the lower 4" of the pot and the upper one over the top 8". The pot itself nests on a 2000 watt hot plate. Thermocouples are placed at the midpoint of each heating element, and are 3" and 9" above the bottom of the pot.

3. Condensing Head.

A non-automatic condensing head was used to determine the boil-up rate as a function of pressure drop across the column. A large cup 1" long by 1" O.D. leading off into 8 mm. tubing was used in this case. All the condensing liquids fell into the cup, the draw-off being regulated by an external stopcock.

In determining the number of theoretical plates an automatic head was used with a draw-off through capillary tubing from a small cup. Figure 4 illustrates this setup. The proportion of liquid drawn off was regulated by a timing mechanism giving a known reflux ratio from which the total boil-up could be calculated.

4. Packing.

The packing for the column is .24" x .24" (i.e. 3/8") protruded #316 stainless steel furnished by the Scientific Development Company, Box 795, State College, Pennsylvania. (See their Bulletin No. 12, Girdler R9.44-2-1).

Packing the column was accomplished by extending a glass tube four feet above the top of the metal tube and filling through the glass tube. All the packing fell at least 4 feet while the column was tapped gently. According to the literature this procedure should give consistent packing. A total of 904 grams of the packing was used, giving a packed density of 18.96 lb. per ft.^{3}.

B. Experimental Data.

1. Determination of Boil-up.

Using methylcyclohexane the boil-up was determined as a function of the back pressure created in the pot. The head temperature during this phase was measured by a thermometer suspended downward through the condenser to a point 1-2" below the cooling jacket. Table I and Figure 4 illustrate the results.

TABLE I.

Boil-Up Versus Pressure Differential.

Barometric Pressure 756.3 mm. Hg.

ΔP "H_2O	Boil-up ml/min., liquid	Linear Velocity Ft./Sec. at Column Temp.	*Head Temp. °C.	Pot Temp. °F.	Remarks
.75	103	.65	99.8	215	
.75	108	.68	99.8	215	
1.00	116.5	.74	99.8	215	
1.25	129.0	.82	99.8	215	
1.50	151.0	.96	99.9	215	
2.00	158.0	1.00	100.0	215	
2.25	162.0	1.13	100.0	215	
2.50	189.0	1.20	100.0	215	
3.00	201.0	1.26	100.2	215	
3.75	234.0	1.48	100.4	215	
4.75	252.0	1.59	100.2	215	
5.50	279.0	1.76	100.3	215	
9.25	276.0	1.73	100.3	215	Head flooding
1.0	116	.74	99.8		This point was checked on the mixture using an automatic head and a reflux ratio of 10:1
13.5	-	-	-	-	Column flooded

* The temperature was measured by a thermometer suspended from the top of the condenser into the cooled portion. A steam correction change as boil-up increased could account for the change in head temperature.

2. Theoretical Plate Determination.

A mixture of methylcyclohexane and n-heptane was used to determine the number of theoretical plates at different linear velocities. A mole ratio of 3 moles methylcyclohexane to 1 mole n-heptane was used, with a total volume of 2392 ml. (1730 ml. methylcyclohexane and 662 ml. n-heptane).

The index of refraction at 20°C. was taken using the sodium D line.

Table II and Figure 5 show the results.

TABLE II.

Theoretical Plates, HETP and Boil-Up.

Barometric Pressure = 758.0 mm. Hg.

54" Column Packing

ΔP "H_2O	Linear Velocity Ft./Sec. at Column Temp.	Theoretical Plates	HETP, Inches	N_D^{20} Pot	N_D^{20} Head
0	-	-	-	1.4133	-
.50	.55	28	1.93	1.4133	1.3915
.50	.55	28	1.93	1.4134	1.3973
1.13	.79	29*	1.86	1.4140	1.3980
1.13	.79	27	2.00	1.4140	1.3995
1.13	.79	27	2.00	1.4143	1.3995
4.50	1.59	23	2.35	1.4150	1.4030
4.50	1.59	23	2.35	1.4150	1.4031

* Equilibrium had not been established at the head.

The theoretical plates were determined by Figure 6 taken from the literature (Ind. Eng. Chem., Anal. Ed. 12, 544, 1940). These determinations were checked by the regular method, using the liquid-vapor diagram for the n-heptane-methylcyclohexane system. If R, the ratio of the vapor pressure of n-heptane to methylcyclohexane is taken as 1.07, then:

$$Y_1 = \frac{1.07}{\frac{1}{X_1} + 1.07 - 1}$$

This equation is valid since the mixture has been shown to be an ideal solution, at least for practical purposes. Y_1 is the mole fraction of n-heptane in the gas phase, while X_1 is the mole fraction of n-heptane in the liquid phase. From this equation the liquid-vapor diagram (Figure 7) may be constructed. The refractive index of n-heptane-methylcyclohexane mixture is given by the following equation:

$$N_D^{20} = 1.4232 - 0.0410X_1 + 0.00555X_1^2$$

Here X_1 is the mole fraction of n-heptane in the liquid. In Figure 8 X_1 is given as a function of N_D^{20}. Values for the pure liquids were in agreement with this equation.

In determining the number of theoretical plates, with pot and head refractive indices, for example, of 1.4133 and 1.3975, respectively, the values of 22 and 50, respectively, are found on Figure 6 corresponding to these refractive indices. The number of plates in the column is then 50-22, or 28, for a column operating on total reflux.

By the more standard procedure, the refractive indices would be converted (Fig. 8) to n-heptane mole fractions of 0.25 and 0.69. Stepping off plates for these values between the operating and equilibrium lines of Figure 7 gives a total of about 27 plates.

The literature provided with the packing gave results obtained with a n-heptane-methylcyclohexane mixture on a column 8.4 ft. high. If these values for pressure drop and theoretical plates at given linear velocities are multiplied by the factor of 0.535 (4.5/8.4) to predict results for the shorter column used in this investigation, the calculated results shown in Figures 4 and 5, and Table II, are obtained.

TABLE III.

Comparison of Actual and Predicted Behavior of Protruded Packing at Various Linear Velocities.

Linear Velocity, Ft./Sec., Column Conditions	Pressure Drop, Inches, H_2O		Theoretical Plates	
	Found	Calculated	Found	Calculated
0.7	0.90	1.45	27.4	27.3
1.0	1.80	2.70	26.2	26.8
1.3	3.05	4.60	24.6	26.3
1.6	4.55	7.30	22.9	25.8

IV. DISCUSSION:

At all linear velocities the pressure drop across the column was less than would be predicted from the literature on the packing. This result may have been due to the efficiency of the cone screen support used for the packing. At relatively low linear velocities the theoretical plates predicted and found are very similar, but at near flooding velocity the theoretical plates found are about 10% less than would be predicted.

REPORT BY: Orin C. Bradley DATE: March 31, 1953
Kenton Atwood

READ AND UNDERSTOOD BY: William M. Keely DATE: March 31, 1953

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FIGURE 1.

Fractionation Column.

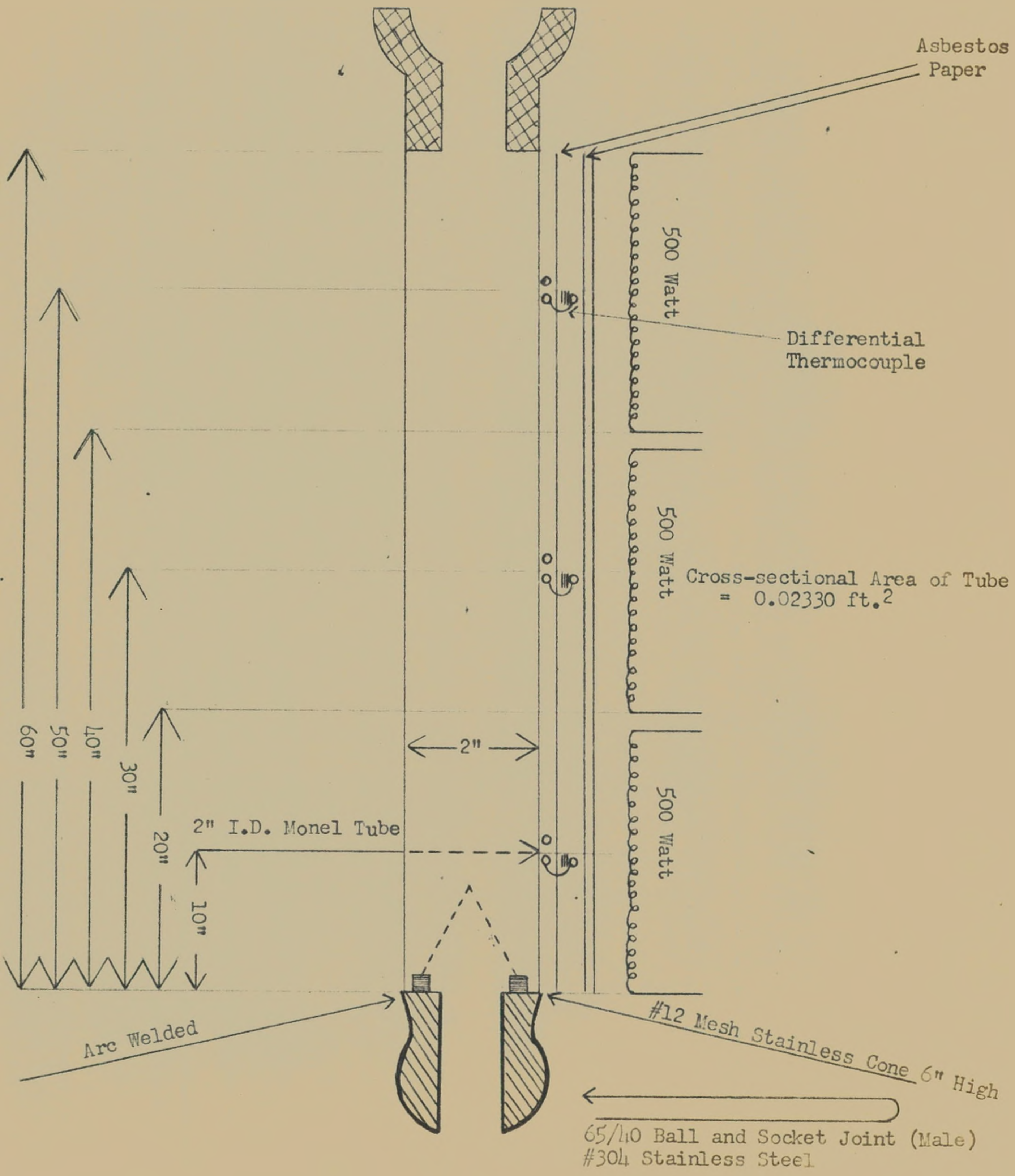
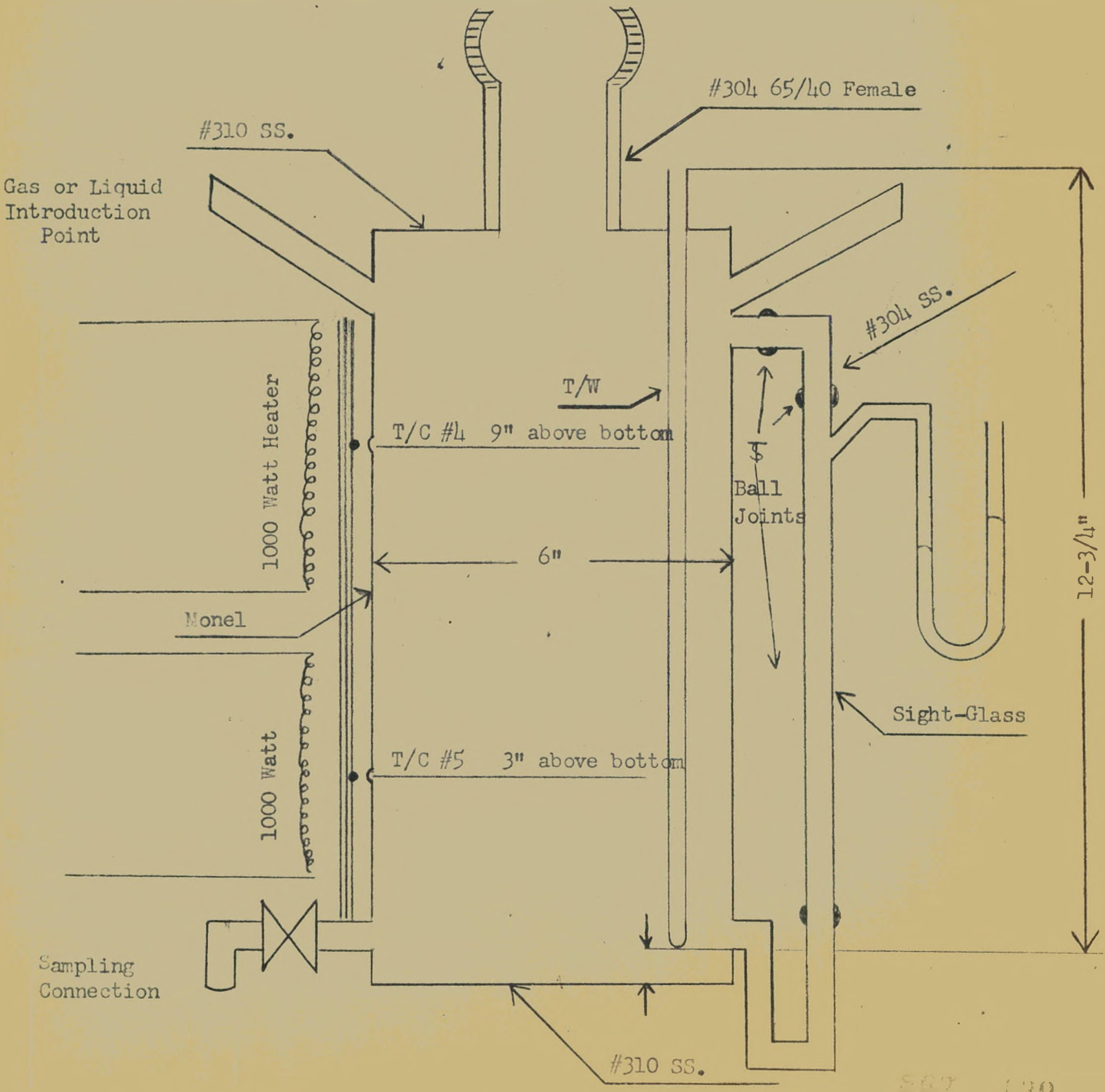


FIGURE 2.

Distillation Pot.

Note: a. All fittings are #304 Stainless Steel
b. Overall length of Pot is 12"
c. Outside Insulation is Asbestocel



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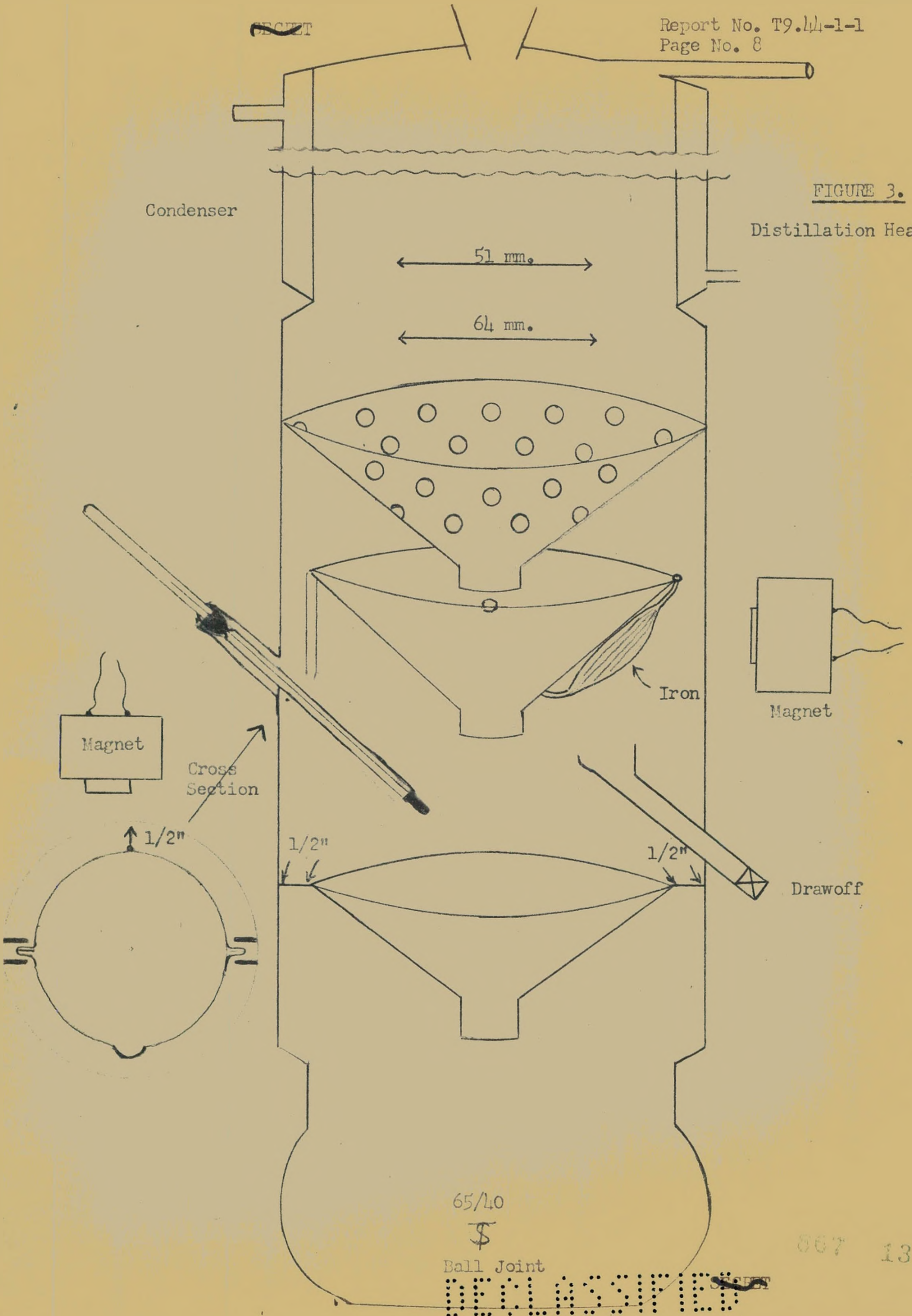

FIGURE 3.

Distillation Head.

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FIG. 4.

Pressure Drop vs. Linear Velocity.

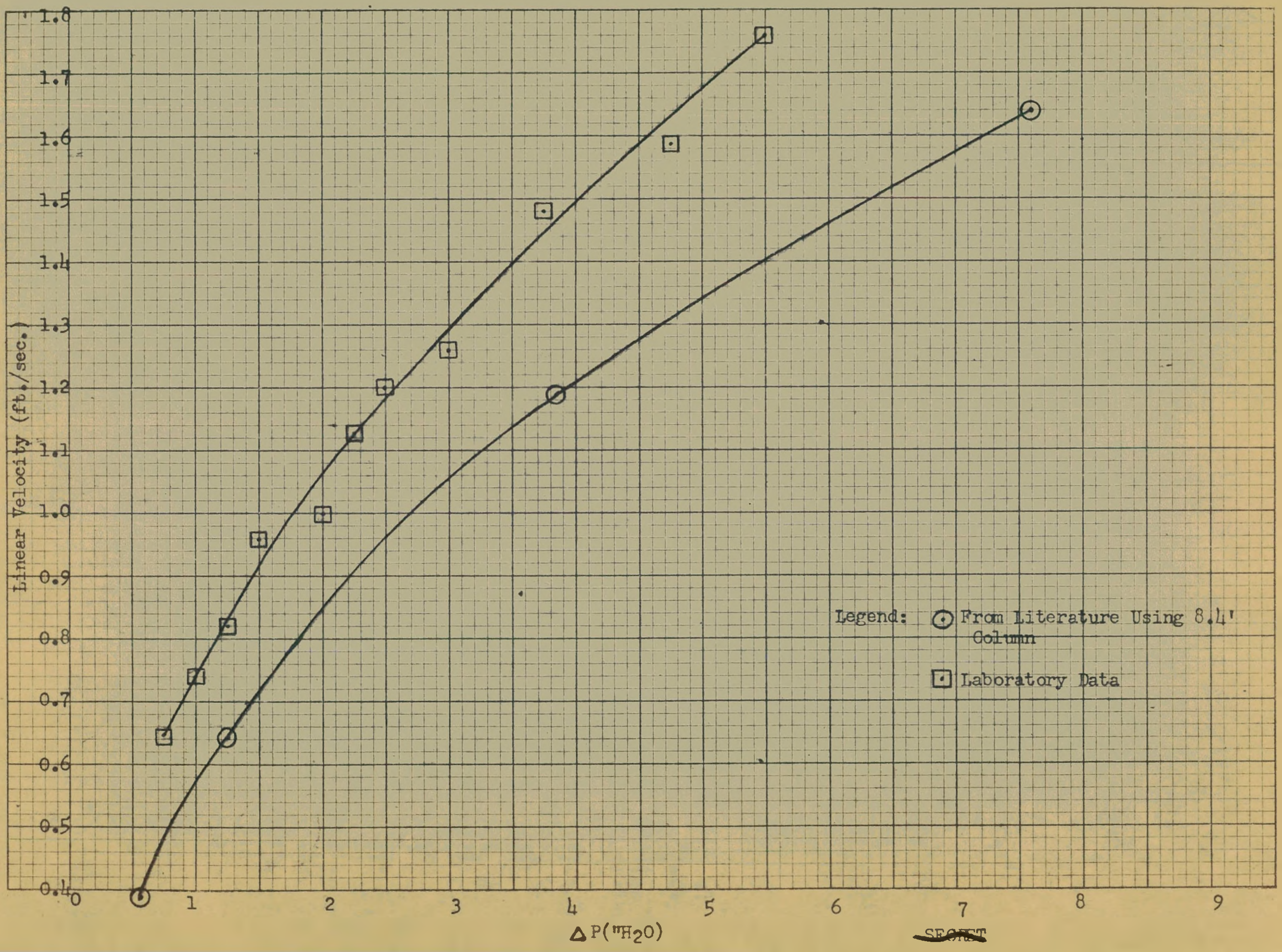

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FIG _ 5.

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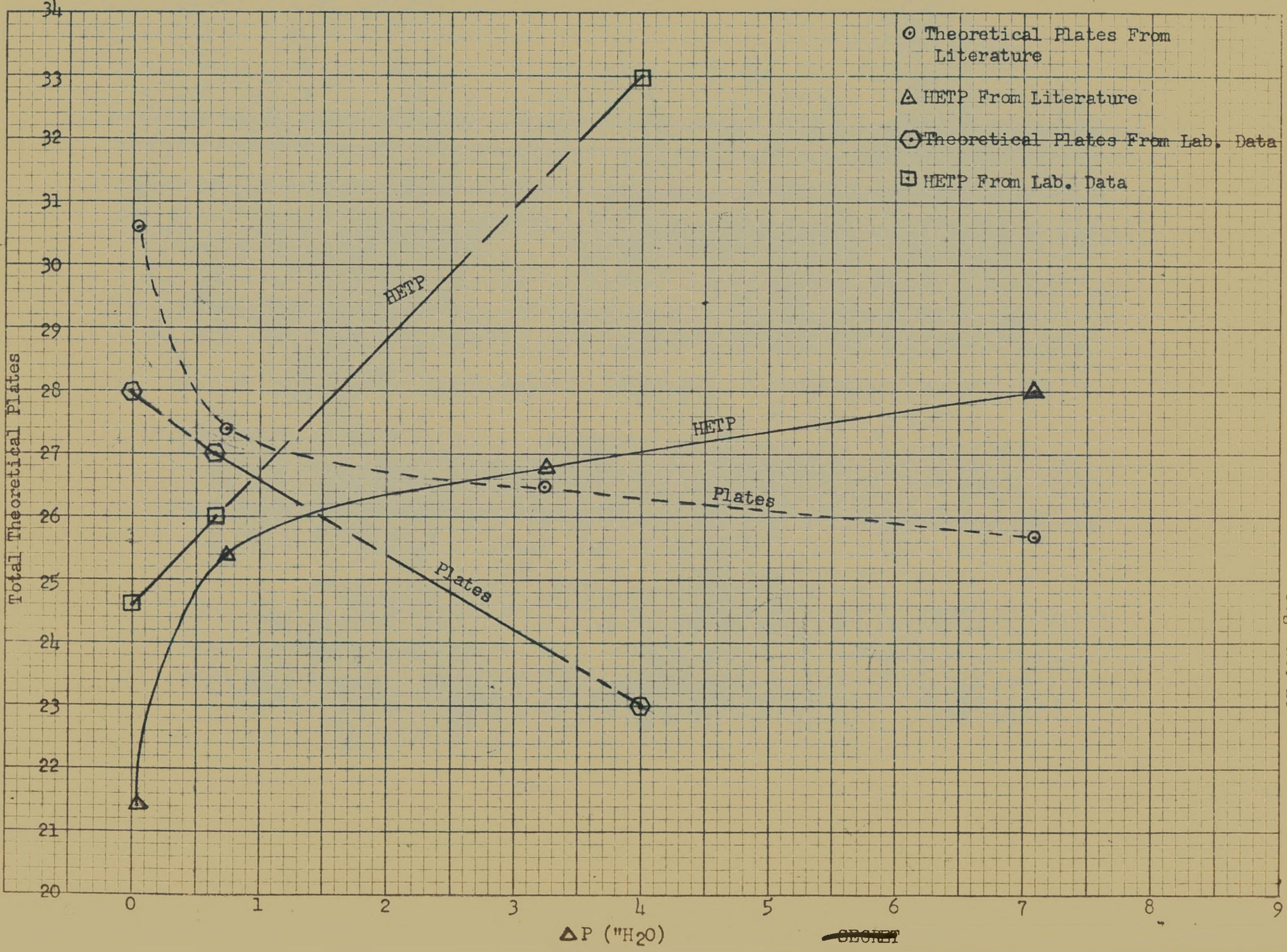
Column Performance.



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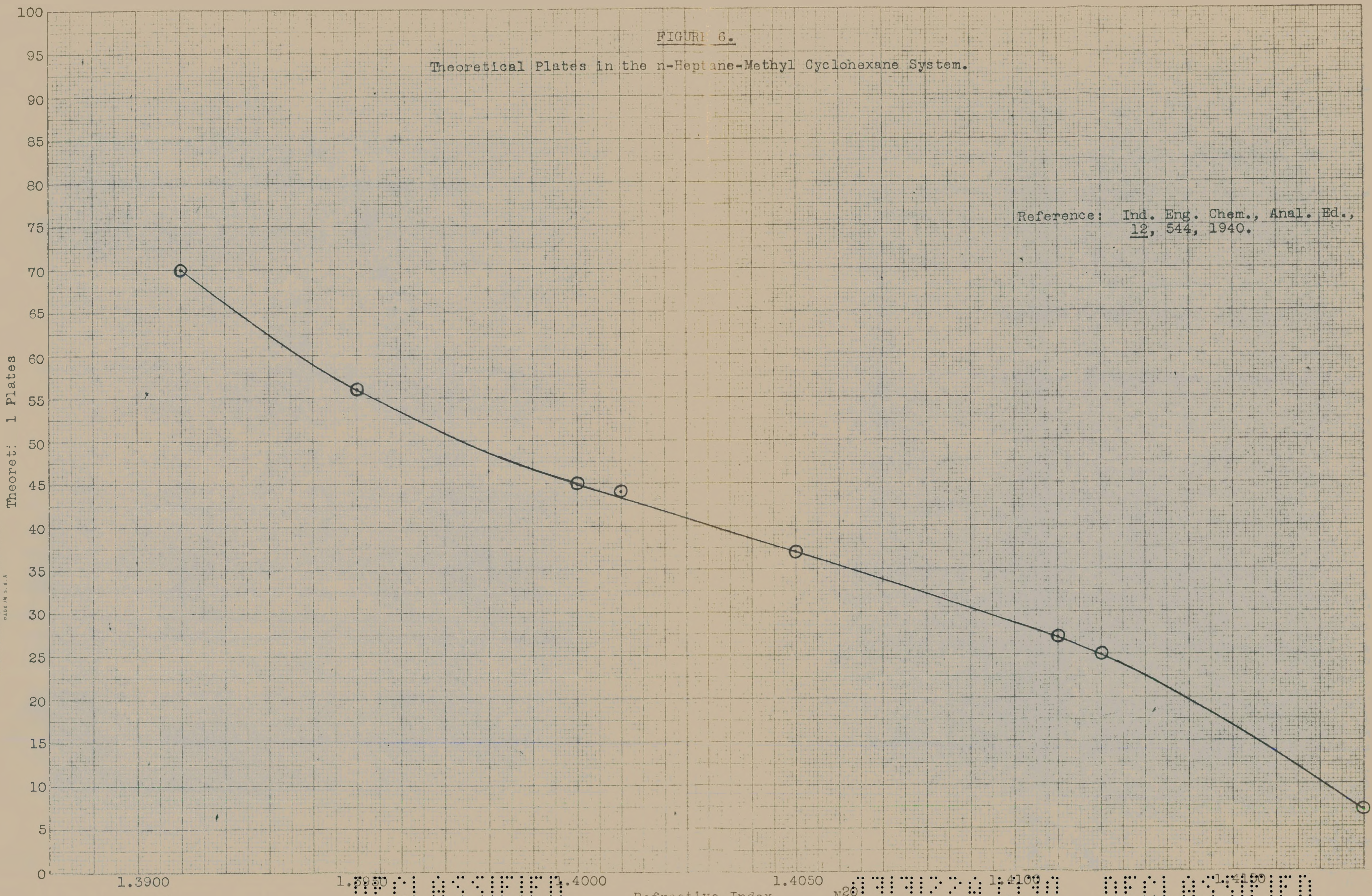

FIGURE 6.

Theoretical Plates in the n-Heptane-Methyl Cyclohexane System.

Reference: Ind. Eng. Chem., Anal. Ed., 12, 544, 1940.

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FIGURE 7.

Equilibrium and Operating Lines For the System n-Heptane-Methyl Cyclohexane.

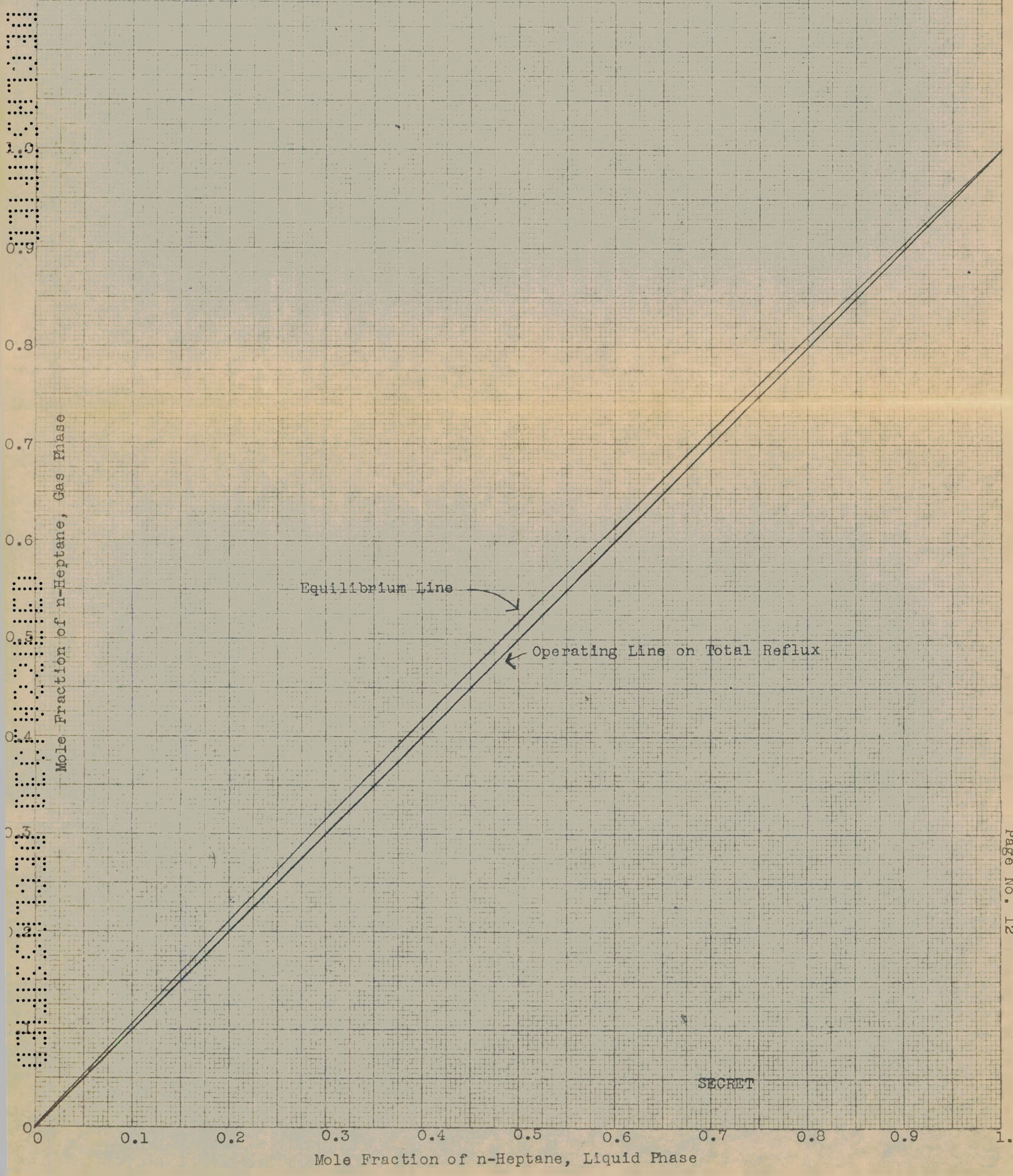

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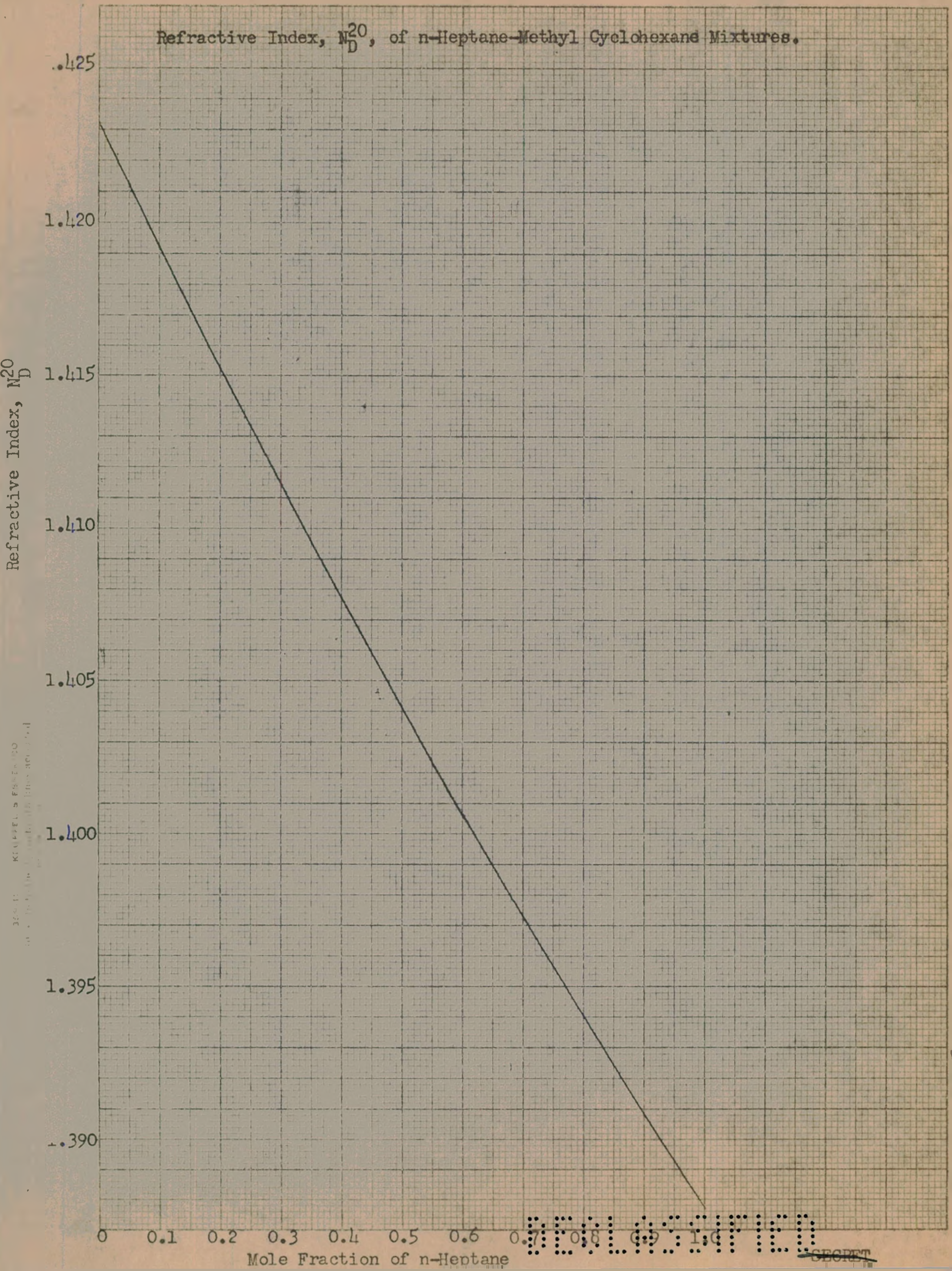
FIGURE 8.



Refractive Index, N_D^{20}, of n-Heptane-Methyl Cyclohexane Mixtures.

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Report No. T8.10-1-2

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THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

THE DECOMPOSITION OF DIMETHYL ETHER-BORON TRIFLUORIDE COMPLEX BOILING IN GLASS EQUIPMENT UNDER ATMOSPHERIC PRESSURE.

March 31, 1953

Work by:

Henry Nevers
W. M. Keely
Kenton Atwood

Report by:

Kenton Atwood

Sentence Summary

The decomposition of dimethyl ether-boron trifluoride complex boiling under atmospheric pressure was studied in glass equipment, in both the absence and presence of added metals.

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I. INTRODUCTION:

Information on the decomposition of the dimethyl ether-boron trifluoride complex (polymer) at the atmospheric boiling temperature (128°C.) was required in connection with Contract No. AT(30-1)-1506 (Job No. 32-4111) for the Atomic Energy Commission. The purpose of this report is to compare the decomposition rate under atmospheric boiling conditions with rates previously obtained for polymer boiling under reduced pressures.

II. SUMMARY OF PREVIOUS WORK:

In Volume 5, Division III of the National Nuclear Energy Series, Manhattan Project Technical Section, the earlier work on the subject is summarized. The original work is mainly reported in Report 100B-R-221 (A-2120). This work indicated that the decomposition reaction was not influenced by a variety of added metals. The addition of water, however, greatly increased the decomposition rate, as did solid corrosion products produced by the action of wet polymer on monel metal.

III. SUMMARY AND CONCLUSIONS:

This investigation, in agreement with earlier work, shows that the decomposition of the dimethyl ether-boron trifluoride reaction is a homogeneous reaction, except that finely divided iron may be a catalyst. The rate of decomposition in a static system from which liquid decomposition products are not allowed to escape is approximately what would be predicted from the work at lower temperatures.

When decomposition products are rapidly removed from the polymer, however, the decomposition rate increases greatly, and this behavior is not at all clearly anticipated by the earlier work. It appears, however, that the concentration of the decomposition products has a very great effect on the reaction, and unless all of these concentrations are accurately measured and the kinetics of the reaction studied in detail it may be very difficult to make predictions of the behavior of polymer under varying conditions in various types of apparatus.

The behavior of polymer stored for over two weeks in sealed tubes at 135°C. indicates that solid formation should not be expected in dry polymer maintained for long periods at the atmospheric boiling point. The formation of gaseous decomposition products in sealed tubes appears to be very limited.

IV. RECOMMENDATIONS:

It is recommended that further work should deal with the quantitative effect of products on the rate of the decomposition reaction. The rate of decomposition at various partial pressures of methyl fluoride would be of particular interest.

V. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL DATA:

Notebook References: Laboratory Book No. 330, pp. 1-58.
Assignment No. A-407.

A. Apparatus.

1. Polymer Preparation System.

The equipment for polymer preparation is shown in Figure 1. Dimethyl ether and boron trifluoride were metered, both at about 1.5 l. per min., into the dried 2 l. flask, which was cooled in acetone kept near room temperature by the addition of small amounts of dry ice. Water cooling was not used because of the danger of explosion if the flask should break.

2. Apparatus for measuring decomposition rates without withdrawal of liquid decomposition products.

This apparatus is shown in Figure 2. In the first run gas was collected over water; in the second over mercury.

3. Apparatus for measuring decomposition rates with withdrawal of all decomposition products.

This equipment is shown in Figure 3.

B. Experimental Data.

1. Polymer decomposition without withdrawal of liquid decomposition products.

Two runs in the equipment of Figure 2 were made; in the first gas was collected over water; in the second it was collected over mercury because of the large solubility of CH_3F in water. In both cases the dried, degassed polymer was introduced into the dried decomposition flask. The polymer was heated to boiling, the dry air in the flask being replaced by polymer vapor, and the rate of gas evolution was measured by drawing off gas into a buret while maintaining constant pressure in the system. A typical plot of gas evolution vs. time is shown in Figure 4. The initial rate is obtained from the slope of the curve after the first few minutes of gas evolution. Solids were added to the decomposition flask through the top stopper while the material in the pot continued to boil.

The results of two runs are shown in Table I. Rates were generally obtained over a period of 1-2 hours, and the rate of gas evolution was generally reasonably constant over these periods. The rates and temperatures given are averages over the time period considered. Measurements were made in consecutive order, and the order of addition of solids is indicated by the appearance of areas under the various headings. That is, in the first run the order was - empty glass reactor, reactor plus powdered glass, this plus 316 SS, then reactor plus glass plus 316 SS plus Monel plus powdered iron plus mercury.

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TABLE I.

Polymer Decomposition Without Withdrawal of Liquid Products.

Surface Areas, Sq. Cm.								
Glass Reactor, Approximate Surface Area	Added Powdered Pyrex, Approx. Surface Area	Monel, Approx. Surface Area	316 SS Approx. Surface Area	Powdered Fe, Approx. Surface Area	Hg, Wt. of Liquid, Gms.	Temp. °C.	Rate of Decomposition, % per Day	Notes
Run No. 1, Gas Collected Over Water, Charge 5.69 Moles of Polymer								
530	0	0	0	0	0	128.5	3.86	
530	0	0	0	0	0	127.9	3.80	
530	13,570	0	0	0	0	127.2	3.30	
530	13,570	0	528	0	0	126.5	2.79	
530	13,570	504	528	4080	195.7	126.5	5.18	Very short run, Plugged gas exit.
530	13,570	504	528	4080	195.7	126.5	7.44	Next day.
530	13,570	504	528	4080	195.7	126.5	7.61	
Run No. 2, Gas Collected Over Mercury, Charge 5.91 moles of Polymer								
530	0	0	0	0	0	129.8	7.14	Bumping
530	0	0	0	0	0	127.6	4.14	Bumping ceases after addition of Hengar Granules
530	0	768	0	0	0	126.5	3.10	
530	0	768	804	0	0	127.7	4.06	Next day.
530	0	768	804	0	0	110.0	0.88	Reduced Pressure
530	0	768	804	4080	0	126.0	5.00	
530	0	768	804	4080	230	126.1	2.11	
530	0	768	804	4080	230	128.5	2.50	Elevated Pressure

2. Polymer decomposition with recirculation of the gaseous decomposition product.

The apparatus of Figure 2 was used in conjunction with a bellows type pump to circulate CH_3F through the system. Leaks in the bellows and other difficulties made it impossible to collect data before it was desirable to study recirculation in a larger unit, and experiments with small glass apparatus were accordingly stopped.

3. Polymer decomposition with rapid withdrawal of both liquid and gaseous decomposition products.

In this experiment (Figure 3) all decomposition products (methyl fluoride and methyl borate-boron trifluoride complex) were rapidly separated from the polymer by distillation. A change of dry polymer was introduced to the dry distillation flask, and rates of gas evolution were measured at various boil-up rates. Liquid was drawn off at the top of the column to maintain the head temperature at around 107°C., and the column itself was maintained at around 128°C. by electrical heaters. The pot temperature was 130°C. Runs at given boil-up rates lasted for about one hour, and the rate of gas evolution was reasonably constant over this period. The amount of polymer in the system was taken as the average amount present during the period of measurement, and this continually reduced because of the continued draw-off required to keep the head temperature high. Data are reported in Table II.

TABLE II.

Polymer Decomposition With Withdrawal of Liquid Products.

Moles of Polymer in System	Boil-up Rate g./min.	Decomposition Rate cc/min.	%/day	Temp. of Vapor in Head, °C.
5.76	4*	27	27	100-114
5.49	11*	33	35	100-114
4.99	17*	43	50	100-114

* Approximate

4. Polymer stability in sealed tubes.

In these experiments about 5 g. of dry polymer were sealed off in 8 mm. tubes with a volume of about 8 cc. Two tubes contained polymer only, and metal packing was added to two others. The tubes were then held (surrounded with iron pipe) in an oven at 135°C. for periods ranging up to 17 days. Tubes were removed from the furnace and cooled to liquid nitrogen temperature before being removed from their protective casings. The tubes were broken while cold, and allowed to warm up while attached to a gas buret. It appeared that less than 1 cc. of gas had been produced in each case, although accurate measurements to determine small amounts of gas production were not made. Data are given in Table III.

TABLE III.

Polymer Stability in Sealed Tubes at 135°C.

Duration of Test, Days	Polymer Wt., g.	Metal Added, g.	Appearance at End of Test
3	4.4	0.0	Clear amber liquid, no solids visible
8	5.5	0.2 (316 SS)	Clear amber liquid, no solids visible
17	5.5	0.0	Clear amber liquid, no solids visible
17	5.4	0.3 (Monel)	Clear amber liquid, no solids visible

5. Decomposition of tetrahydrofuran-boron trifluoride complex.

About 3 moles of this material, a possible substitute for the dimethyl ether-boron trifluoride complex, were prepared by passing BF_3 through tetrahydrofuran and degassing the resultant product under vacuum after an excess of BF_3 had been added. The decomposition was then studied in the apparatus of Figure 2. The highest temperature reached in boiling under atmospheric pressure was 181°C.; the temperature fell to 163°C. in a little over an hour of boiling. Gas evolution was very copious, and yellow oil was produced in the condenser. At the end of the run the residue in the pot resembled a black, viscous tar on cooling to room temperature; decomposition of the tetrahydrofuran-boron trifluoride complex had evidently been very extensive.

6. Measurement of decomposition rate.

Decomposition rates were calculated from the rate of gas evolution assuming the decomposition reaction to be:

$$3(CH_3)_2O\cdot BF_3 = (CH_3O)_3B\cdot 2BF_3 + 3CH_3F$$

Volumes were calculated from the ideal gas laws, and an allowance of 10 mm. Hg for the vapor pressure of the complex.

VI. DISCUSSION:

The main difference between the first and second runs of Table I is the slower rate in the first part of the first run, and this may be due to an initial uptake of CH_3F in the water. In the first part of the first run the boiling rate was increased about 50% without any noticeable effect on decomposition rate.

There were no indications of heterogeneous reaction except when powdered iron was added. Gas from the second run after iron addition was tested somewhat qualitatively for H_2, and was found to contain 5-10%, indicating possible reaction of the iron. After iron addition there was considerable bumping, and this ceased and the rate of gas evolution went back to normal on addition of the mercury. This suggested that superheating under solid iron stuck to the flask may have been responsible for the rapid gas evolution, rather than catalysis. In the first run the presence of mercury did not prevent a fast gas evolution, but in this case a great mass of powdered glass was present also, and in spite of the mercury superheating may have been going on under a paste of glass and powdered iron.

It appears probable that some reduction of reaction rate because of decomposition product accumulation in the pot is taking place. In Run No. 2 corrections for the temperature lowering from 129.8 to 127.7°C. are made using the slope of the decomposition rate vs. reciprocal temperature curve previously reported and in Table IV decomposition rates vs. percentage of total decomposition of polymer are given; similar results for A.E.C. run No. 31 (A-2120) are also shown.

TABLE IV.

Decomposition of Polymer as a Function of Amount Decomposed.

Percentage of Initial Rate of Decomposition	Total Percent Decomposed
Run No. 2	
100	0.00
75	0.38
63	0.52
A.E.C. Run No. 31 (Report No. A-2120)	
100	0.000
84	0.065
57	0.080

It may be noted that the rate of reduction in decomposition rate is much more sharp in the A.E.C. run than in ours, which is probably because only the liquid decomposition products accumulate in our apparatus, while all of the products accumulated in the other apparatus. The rate reduction could be due to a close approach to equilibrium, or to an inhibiting effect of decomposition products on the rate of the decomposition reaction.

At the time that the run at 110°C. (Table I, Run No. 2) was made, the rate of decomposition had declined to 63% of its initial value, after correction for the small temperature drop was made. If this correction factor is applied (0.63) to the rate at 110°C., a value of 1.22% per day is obtained as the predicted initial rate if the experiment had been started at 110°C. If this is compared with the initial rate of 7.14% per day at 129.8°C., the following equation is obtained:

$$\log R_{(\%\ \text{per day})} = \frac{-5990}{T(^\circ\text{K.})} + 15.71$$

This compares with the equation obtained in the earlier work:

$$\log R_{(\%\ \text{per day})} = \frac{-7555}{T} + 19.75$$

The equations appear to be different, but the main difference is in the slope of the log R vs. 1/T curve, and considering the difference in apparatus and the nature of the measurements this is not very great. In Table V are results predicted from the two equations, and from our value at 128°C., assuming the slope of the earlier work.

TABLE V.

Polymer Decomposition Rates Predicted At Various Temperatures.

T, °C.	Decomposition Rate, % per Day Our Equation	Equation from Earlier Work (A-2120)	Slope From Earlier Work (A-2120), Our Rate at 128°C.
110	1.22	1.07	0.72
128	5.6	8.3	5.6
134	9.3	15.9	10.8

Considering that the rates in individual experiments previously reported vary by close to a factor of two, the agreement of these results looks reasonable.

From Table II it is evident that the removal of all decomposition products greatly increases the decomposition rate, and this rate increases with boil-up. This observation does not seem in agreement with the fact that an increase in boiling rate of 50% did not increase the decomposition rate measured in the apparatus of Figure 2. The explanation might be found, however, in a faster return of dissolved CH_3F to the system operating with no distillation column. Another possibility is that a correct value for the initial decomposition rate (Figure 4) was not obtained. The rapid evolution of gas in the first minutes of the run may have represented actual decomposition rather than expulsion of air from the system. In any event it is exceedingly difficult to measure the initial rate of a reaction in which the products strongly influence reaction rate, particularly when the reaction considered is rapid.

The results of the earlier work at temperatures below 113°C. tended to indicate that initial decomposition rates measured in a static system (without removal of decomposition products) were very similar to rates measured in a system with a Stedman-packed distillation column to remove these products. Agreement between individual runs was not, however, very close, and one run made at the highest temperature used in the earlier work (113°C.) gave an unusually high decomposition rate in the Stedman-packed column.

REPORT BY: Kenton Atwood DATE: April 1, 1953

READ AND UNDERSTOOD BY: William M Keely DATE: April 1, 1953

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FIGURE

Polymer Preparation Unit.

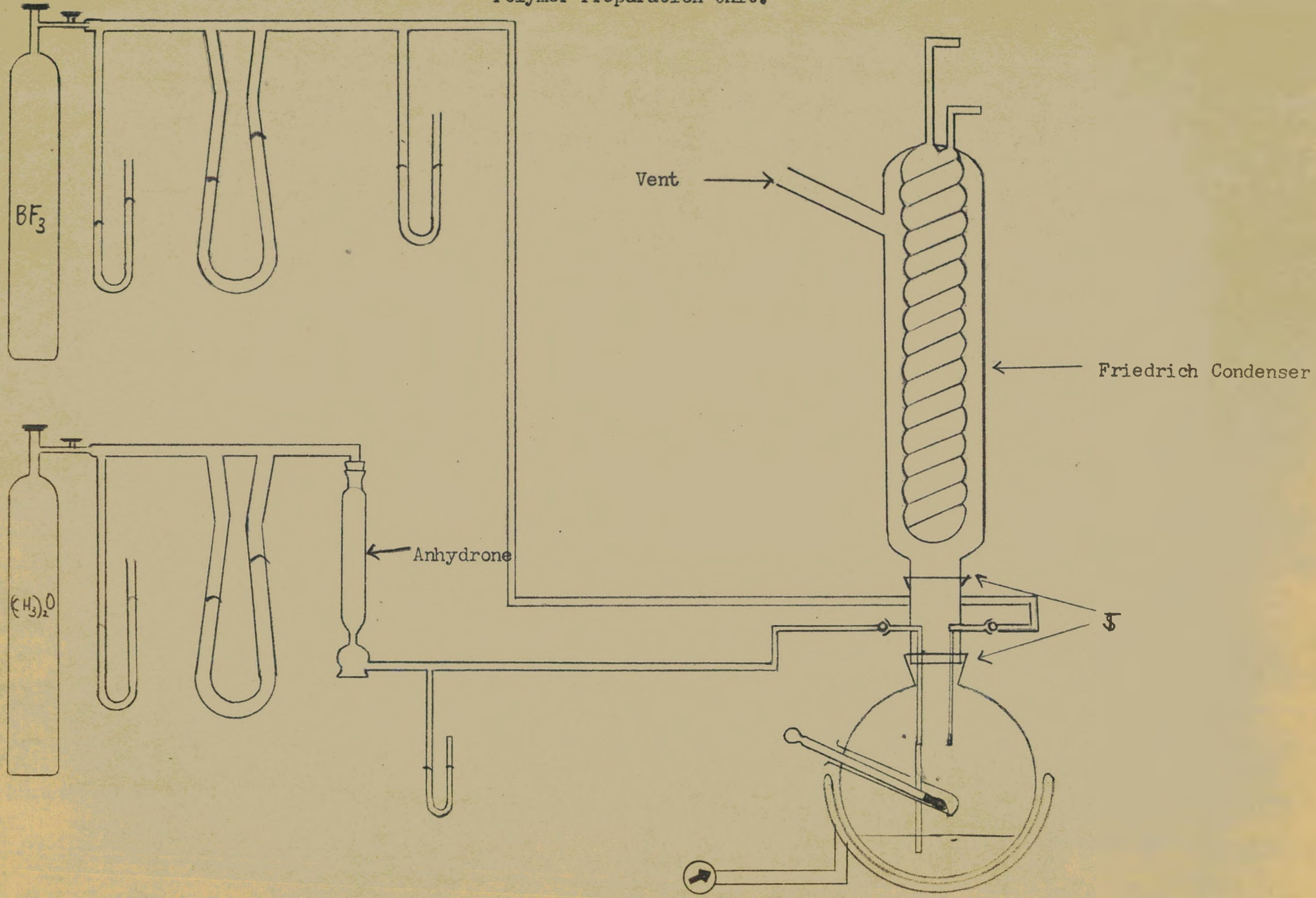

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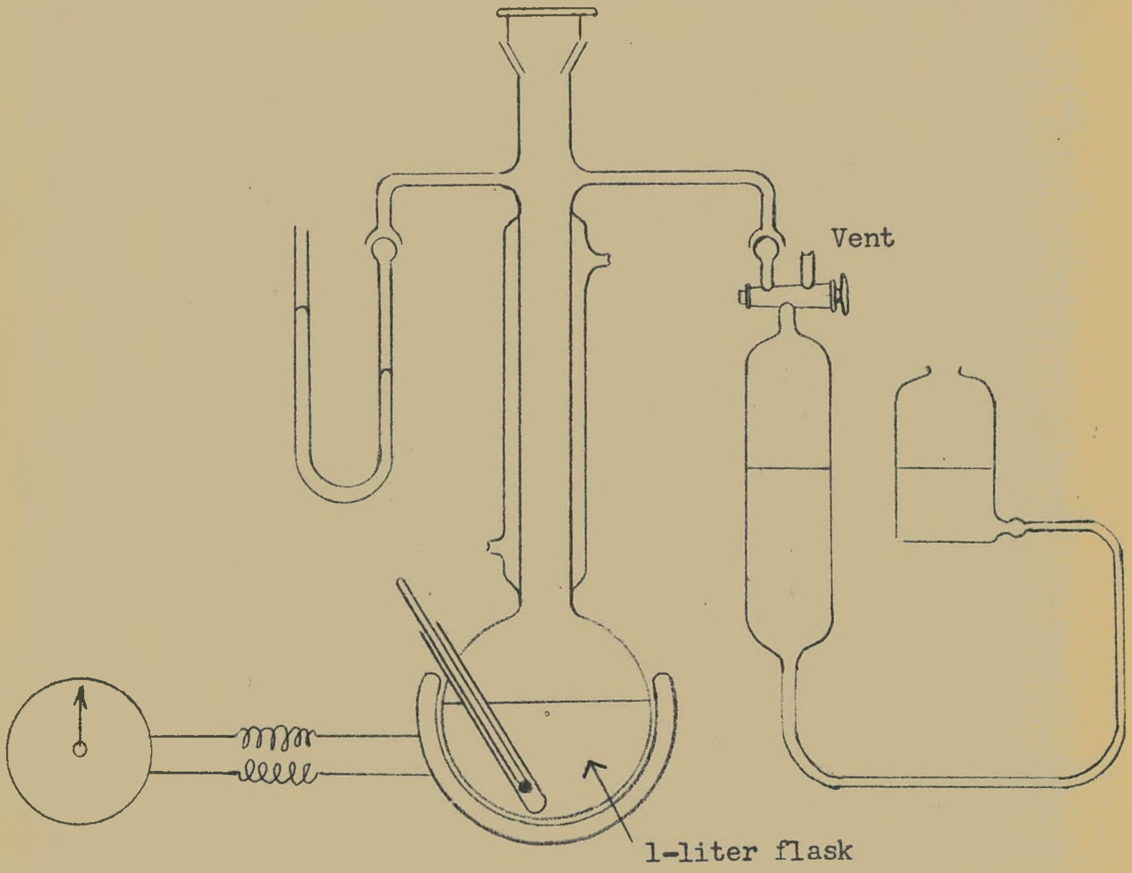
FIGURE 2.

Polymer Decomposition Apparatus.



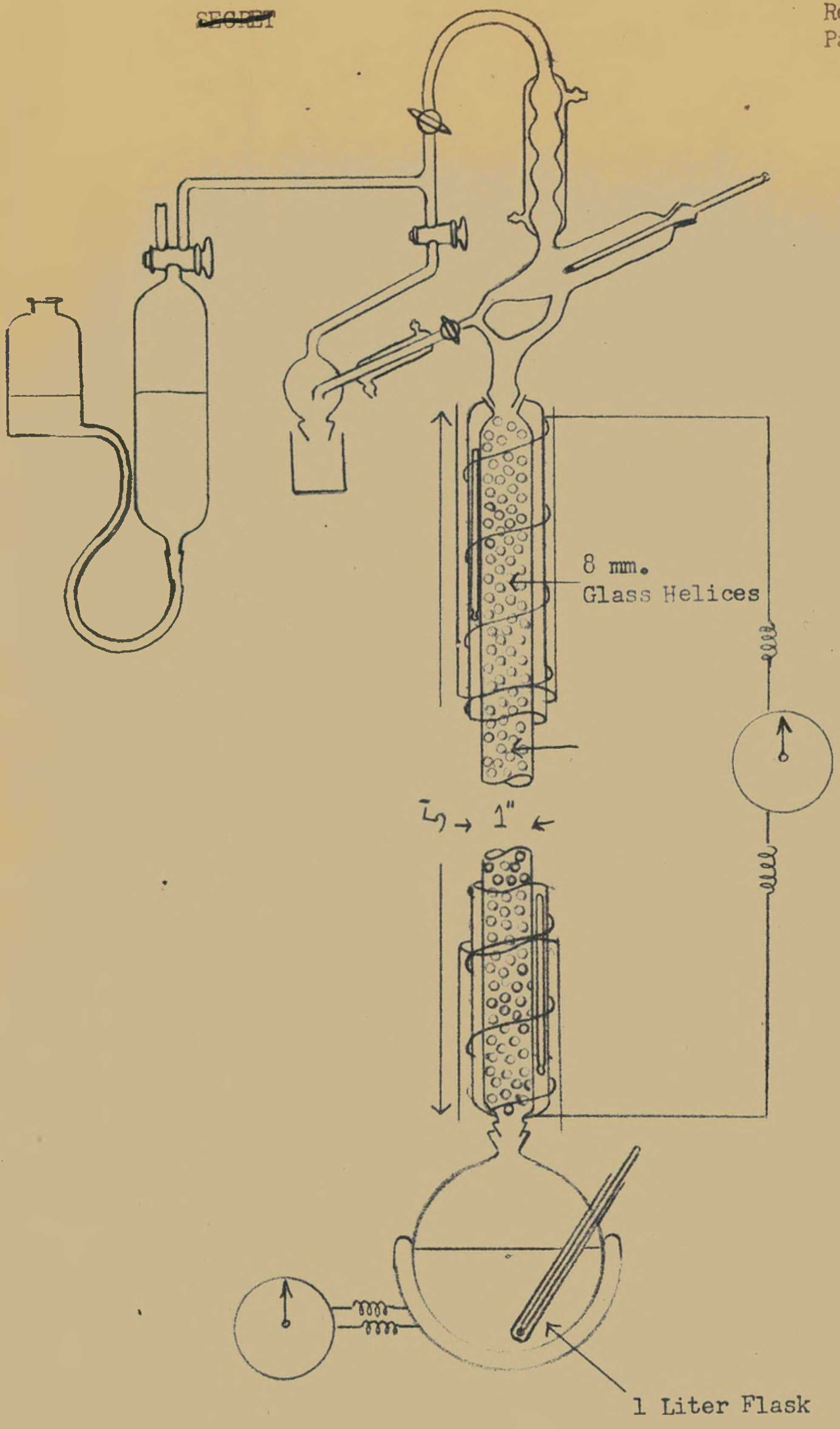
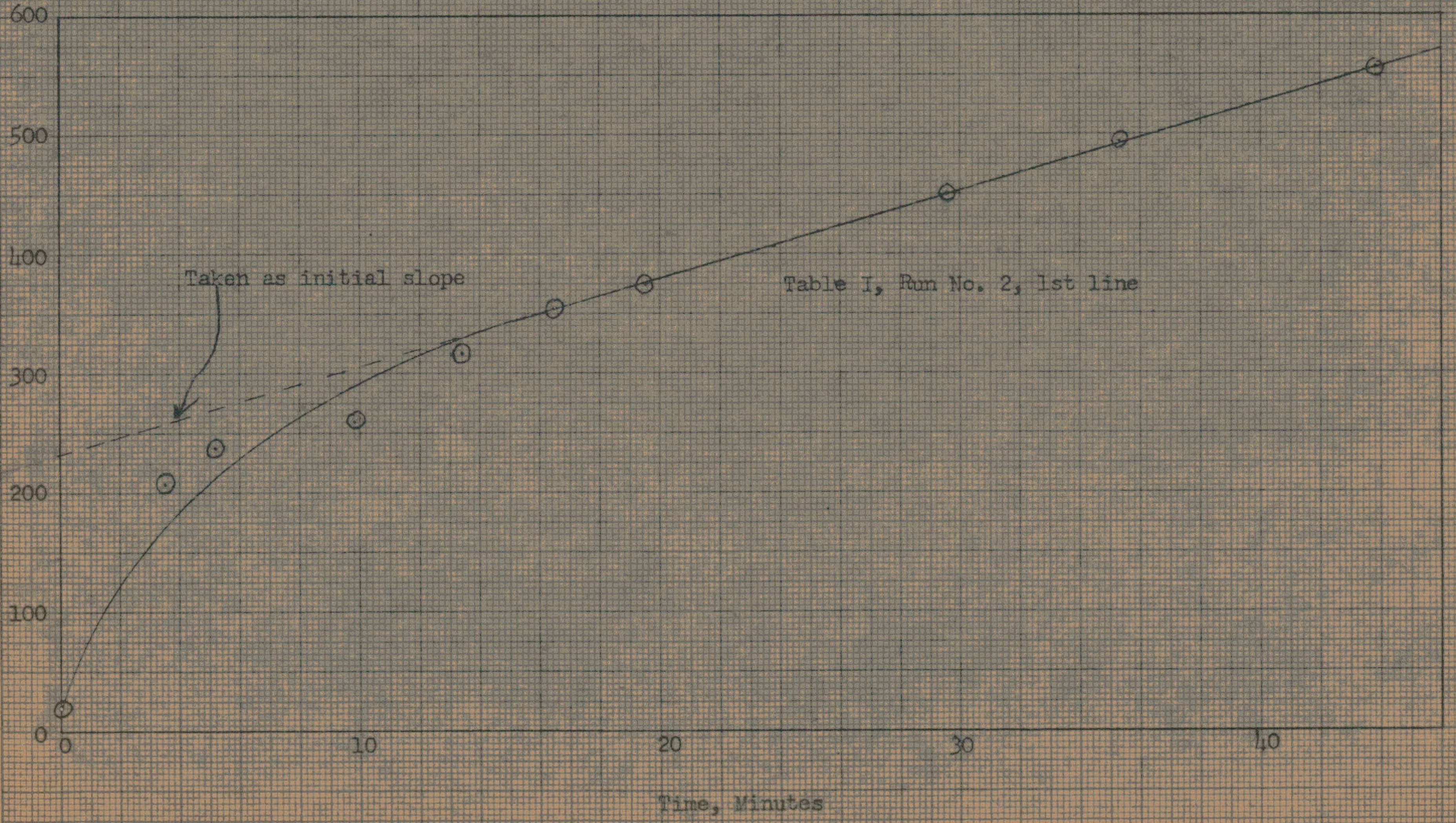


FIGURE 3.

Glass Distillation Column for Polymer Decomposition.

FIGURE 4.

Gas Evolution In Polymer Decomposition.



Report No. T9.40-2-1

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THE GIRDLER CORPORATION
GAS PROCESSES DIVISION
PROCESS DEVELOPMENT AND RESEARCH LABORATORIES
LOUISVILLE, KENTUCKY

SEPARATION OF THE BORON ISOTOPES. Progress Report No. 1.

April 1, 1953

Work by:

O. C. Bradley
Henry Nevers
W. M. Keely
H. W. Fleming
Kenton Atwood

Report by:

Kenton Atwood

Sentence Summary

This report summarizes laboratory work on the problem of separating the boron isotopes.

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I. INTRODUCTION:

In 1943 research on methods of production of crystalline boron in the form of the light isotope, B^{10}, was initiated at Columbia University under OSRD Contract OEMsr-412. The most promising method for isotope separation discovered involved the fractionation of the dimethyl ether-boron trifluoride complex, $(CH_3)_2O \cdot BF_3$, in a distillation column. This method is considered to be effective not because of differing relative volatilities of complex (called "polymer") containing one or the other isotopes, but because the reaction

$$B^{10}F_{3(gas)} + (CH_3)_2O \cdot B''F_{3(liq.)} = B''F_{3(gas)} + (CH_3)_2O \cdot B^{10}F_{3(liq.)}$$

favors concentration of $B''F_3$ in the gas phase. Since the vapor of $(CH_3)_2O \cdot BF_3$ appears to be about 60% dissociated at all temperatures in the gas phase, refluxing polymer in a distillation column tends to concentrate polymer rich in B^{10} in the pot, and polymer rich in B'' in the top of the column.

Once polymer with boron of the desired isotopic ratio is obtained, BF_3 may be liberated by the following reactions:

$$CaF_{2(solid)} + (CH_3)_2O \cdot BF_{3(liq.)} = CaF_2 \cdot BF_{3(solid)} + (CH_3)_2O_{(gas)}$$

$$CaF_2 \cdot BF_{3(solid)} \overset{500^\circ C.}{=} CaF_{2(solid)} + BF_{3(gas)}$$

Although elemental boron may be prepared by the reduction of BF_3, it was found desirable to convert BF_3 to BCl_3 before reduction of the latter compound with H_2.

$$AlCl_{3(solid)} + BF_{3(gas)} = BCl_{3(gas)} + AlF_{3(solid)}$$

$$BCl_{3(gas)} + 3/2\ H_2 = B_{(solid)} + 3HCl_{(gas)}$$

A commercial plant utilizing the reactions given above for the production of crystalline boron rich in the light isotope was designed and constructed by the Standard Oil Company of Indiana, and successfully operated in the first half of 1945. Since that time the plant has gone out of operation.

The Atomic Energy Commission now may desire to resume production of the light boron isotope, and under AEC Contract AT(30-1)-1506 The Girdler Corporation has undertaken design and related work on a new plant for producing the material, since the capacity of the original plant is smaller than the desired production. Due to the extremely great cost of the boron produced in the previous commercial operations, it is very desirable that the new plant be designed to reduce the production costs whenever this is possible. The greater part of the cost of preparing B^{10} previously was in the step of concentrating the isotope in the polymer, and accordingly attention was first directed to reducing the expense of that process.

At temperatures above 80°C. polymer decomposes noticeably according to the reaction:

$$3(CH_3)_2O\cdot BF_3 = (CH_3O)_3B\cdot 2BF_3 + 3CH_3F$$

This reaction appears to be homogeneous, but it is catalyzed by small amounts of water and by corrosion products of the action of moist polymer on metals. The decomposition rate increases with temperature, and it has been thought that at the atmospheric boiling temperature of the polymer (128°C.) the decomposition reaction would be too rapid to allow operation of a distillation column for separation of the boron isotopes. Accordingly the plant operated by the Standard Oil Company of Indiana was run under vacuum at relatively low temperatures. As a result the distillation column had to be much larger than would be required for atmospheric operation, and operational difficulties due to leaks were very great. Air leaking into the system brought in water which caused corrosion. Accordingly the main object of the present laboratory work has been to determine whether or not operations at atmospheric pressure are practical. For successful operation it is required that the column have a satisfactory fractionation factor for the boron isotopes, that the rate of decomposition of polymer not be too rapid, and that materials of construction will not break down under operating conditions.

The fractionation of the boron isotopes at atmospheric pressure was tested by distilling polymer in a two inch monel metal column which had been characterized with a n-heptane-methyl cyclohexane mixture.

Decomposition rates were first run in small glass equipment to determine immediately if the prospects for atmospheric separation were at all promising from this standpoint, and various metals were tested for catalytic effects. Decomposition rates were measured in the metal distillation column, as well as in a small glass column to differentiate between the effects of materials of construction and type of equipment on decomposition rate. The effect on decomposition rate of recirculation of methyl fluoride, one of the decomposition products, was tested. Recirculation of this non-condensible gas might logically be expected to reduce the decomposition of polymer, both by reducing the partial pressure of polymer and by inhibiting or reversing the decomposition reaction. Polymer was held for over two weeks in sealed glass tubes at 135°C. to show up undesirable solid products of secondary decomposition reactions.

Since water strongly increases the corrosive action of polymer, as well as the decomposition rate, it was desirable to investigate the removal of traces of water from the dimethyl ether which is used to produce polymer. Various materials of construction were tested for resistance to polymer at its atmospheric boiling temperature.

Another compound, the tetrahydrofuran-boron trifluoride complex, is known to dissociate to a greater extent than polymer, and might be considered as a substitute for polymer if it were stable at its boiling point. Preliminary tests of the stability of this compound at its atmospheric boiling point were therefore made.

Although the concentration of B^{10} in polymer was a very costly operation in the previous plant operations, the preparation of crystalline boron from polymer also proved to be very expensive. Although no laboratory work was done on this problem, a brief literature search was made, and some suggestions for future work which might lead to improvements in the process are made in this report.

II. SUMMARY OF PREVIOUS WORK:

The earlier work is summarized in "Separation of the Boron Isotopes", National Nuclear Energy Series, Manhattan Project Technical Section, Division III, Volume 5. Much of the original work is reported in Report 100B-R-221 (A-2120).

III. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS:

Conclusions are given in numerical order, and at the end of each conclusion the reference to the Girdler report in which the experiments are described. Since much of the work is incomplete recommendations are given where the indicated conclusions require further substantiation.

1. The rate of polymer decomposition is probably too high to allow operation of a boron isotope separation column at the atmospheric boiling temperature. (T8.10-1-2, this report).

2. The rate of polymer decomposition is strongly affected by the concentrations of decomposition products. (T8.10-1-2, this report).

3. Recirculation of methyl fluoride appears to suppress polymer decomposition in a distillation column. Measurements are required on this effect in the nearly complete absence of methyl borate complex in the recirculated gas. (This report).

4. Monel metal and 316 SS do not appear to affect the rate of polymer decomposition, although powdered iron may increase the rate (T8.10-1-2).

5. Brass and stoneware packings are resistant, at least during short tests, to the action of polymer boiling at atmospheric pressure. More work along this line is required. (T9.35.0-1-1).

6. Dimethyl ether can apparently be dehydrated with activated alumina, but more work, particularly on regeneration, is required on this problem. (T1.25-4-1).

7. Polymer does not yield visible solid decomposition products after more than two weeks in sealed glass tubes, both in the presence and absence of monel metal and 316 SS. Similar experiments are recommended for mixtures of polymer and methyl borate complex. (T8.10-1-2).

8. The two inch distillation column packed with protruded metal packing behaves normally for the separation of n-heptane and methyl cyclohexane. (T9.44-1-1).

9. The tetrahydrofuran-boron trifluoride complex is probably unsuitable for use in separating boron isotopes, at least for distillation at the atmospheric boiling point. (T8.10-1-2).

10. A few suggestions for laboratory work which might lead to improvements in the process for producing elemental boron are given. (This report).

At this time no measurements of the fractionation factors for boron isotopes are available, and this vital question must be settled in further work on whatever system is deemed to be operable from other considerations.

IV. INVESTIGATIONAL PROCEDURE AND EXPERIMENTAL DATA:

Notebook Reference: Laboratory Notebook No. 331, pp. 4-7.
Assignment No. A-407.

The kettle, column, and head used in this investigation are described in Report No. T9.44-1-1. The electrical heaters were used in the first run, but when it appeared that extreme superheating might be possible, the metal distillation pot was heated by immersion in an oil bath.

Polymer, previously prepared and degassed (Report No. T8.10-1-2) was loaded into the dry distillation pot. The liquid was brought to boiling temperature, and the reflux ratio at the top of the column adjusted to give a head temperature indicating 25 mole % methyl borate-boron trifluoride complex at the top of the column. Gas evolution from the column was measured and decomposition rate calculated on the assumption that this gas was methyl fluoride containing polymer and methyl borate complex at 10 mm. of Hg pressure.

Table I and II show decomposition rates as a function of boil-up in both the electrically heated and oil bath heated systems. Table III shows rates with recirculation of methyl fluoride by a Ford fuel pump. Polymer and methyl borate complex vapor were not removed from the recirculating gas.

TABLE I.

Atmospheric Distillation in Metal Column With Electrically Heated Kettle

Run No.	Grams of Polymer in System	Boil-up Rate g./min.	Decomposition Rate		Temp of Vapor in Head, °F.
			cc./min.	%/Day	
1	3063	53	207	44	226
2	3063	53	222	48	226
3	3063	53	219	47	226
4	3063	53	240	51	226
5	3673	12	94	17	226
6	3673	-	184	33	230
7	3673	-	177	32	230

TABLE II.

Atmospheric Distillation in Metal Column With Kettle Heated by Oil Bath

Run No.	Grams of Polymer in System	Boil-up Rate g./min.	Decomposition Rate cc/min.	Decomposition Rate %/Day	Temp. of Vapor in Head, °F.
1	3444	47.6	249	47	230
2	-	61.5	284	54	228
3	-	66.2	280	53	226
4	-	58.3	270	51	230

TABLE III.

Atmospheric Distillation in Metal Column with Kettle Heated by Oil Bath and Recirculation of Methyl Fluoride.

Run No.	Grams of Polymer in System	Recycle Rate of CH_3F, cc/min.	Boil-up Rate g/min.	Boil-up Rate cc/min.	Decomp. Rate cc/min.	Decomp. Rate %/Day	Temp. of Vapor, °F. Head	Temp. of Vapor, °F. Kettle
1	-	none	45	11,600	270	59	225	262
2	3038	1400	45	11,600	155	34	221	258
3	3038	3700	45	11,600	50	11	-	255
4	-	4260	45	11,600	35	8	-	254
5	-	4200	45	11,600	37	8	-	254
6	3038	6400	45	11,600	*	*	239	252

* Apparently no CH_3F produced.

V. DISCUSSION:

The similar decomposition rates shown in Tables I and II indicate that there was no decomposition due to superheating in the first experiments with electrical heating. In the oil bath experiments there is a large temperature drop from the oil to the surface of the metal shell, and another drop from the shell to the boiling liquid. It is indicated that the over-all heat transfer coefficient from metal to boiling polymer is about 100 Btu per hr. per sq. ft., °F., which is reasonable. If steam coils were used to supply heat very little reduction in the overall coefficient would be needed to take care of the transfer of heat from the condensing steam to the metal surface.

Recirculation of CH_3F (Table III) appears to reduce the decomposition of polymer. The amount of methyl borate complex recirculated was not negligible, however, and since such recirculation could not be tolerated in an isotope separation it cannot be positively concluded that CH_3F recirculation itself affords any reduction in decomposition rate greater than might be expected on the basis of the temperature reduction.

VI. PREPARATION OF ELEMENTAL BORON:

From the literature on boron production, it is evident that there has been great difficulty in obtaining pure boron in any form, especially the pure crystalline form. It is therefore probable that the development of new methods for preparing pure crystalline boron would be very time consuming, with doubtful assurance of commercial success. If boron is to be produced on a large scale in the near future it would seem necessary to employ some previously proved method. A process for the preparation of pure crystalline boron through the reduction of BCl_3 with H_2 has already been proved in the plant operated by the Standard Oil Company of Indiana. An electrolytic method (Report No. T8.10-1-1) is said to be commercially successful, but the exact status of the method requires verification.

At the present time design work is being concentrated on the production of crystalline boron by the reaction of BCl_3 with H_2. One of the chief practical difficulties in the process is the removal of HCl from the product gas mixture of H_2 and unreacted BCl_3. Since the equilibrium in the reaction is somewhat unfavorable for boron production, HCl must be continuously removed before the residue of H_2 and BCl_3 is recycled. Separation by refrigeration may be used but is very costly.

One possible method for separating HCl from BCl_3 and H_2 is the reaction of HCl with metals to yield a metal chloride and H_2. Anhydrous HCl does not react with most metals at room temperature, however, with the possible exception of aluminum (Corrosion Reporter, I, No. 4 (Oct., 1946) (Girdler R9.28-7-8); Bull. soc. chim., 576, 768-75). Powdered aluminum is said to be unaffected by cold, dry HCl unless it has been previously heated in H_2 at 300°C., and once started the reaction proceeds spontaneously (Mellor, "Inorganic Chemistry", Vol. 5, p. 209). Although BCl_3 will react with aluminum at high temperatures, it is possible that no reaction would take place at room temperature. Zinc dust does not react with BCl_3 at 200°C. (Mellor, "Inorganic Chemistry", Vol. 5, p. 133), but gaseous hydrogen halides attack zinc and cadmium at moderate temperatures. Cadmium reacts almost completely with dry HCl at 440°C. (Mellor, "Inorganic Chemistry", Vol. 4, p. 476). Although dry liquid HCl does not attack iron, there is a reaction between dry HCl and red hot iron filings (Mellor, "Inorganic Chemistry", Vol. 13, p. 315). Metals such as aluminum, zinc, or cadmium are probably worthy of brief study as agents for separating HCl from BCl_3, although it would not be surprising is these two gases could not be separated by this method.

Solvents which would be used to remove HCl from BCl_3 are limited by the fact that both gases are very strong acids. From steric considerations it appears possible that tertiary amines such as triethanolamine might react with HCl more readily than BCl_3. One literature reference (Report No. T8.10-1-1) may support this assumption.

VII. EQUILIBRIUM DIAGRAM FOR BORON ISOTOPE SEPARATION IN A POLYMER SYSTEM:

For calculations on the separation of boron isotopes in a polymer distillation system it may be assumed that two liquids are being separated, the more volatile having a relative volatility of R with respect to the other component. Then, assuming an ideal solution:

$$Y_1 = \frac{R}{\frac{1}{x_1} + R-1}$$

is the equilibrium equation where Y_1 is the mole fraction of the more volatile component in the gas phase and x_1 is the mole fraction of the same component in the liquid phase. In this case the polymer containing B" is the more volatile component. Figure 1 is constructed using a value of 1.016 for R.

Figure 1 is constructed in sectional strips, with the 45° line drawn under the equilibrium line. The paper should be held in the direction of the printed coordinates. A numbered point on the 45° line has the value indicated for liquid and vapor mole fraction (N_L, N_G).

REPORT BY: Kenton Atwood DATE: April 2, 1953

READ AND UNDERSTOOD BY: William M Kelly DATE: April 2, 1953

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FIGURE 1.

Equilibrium Diagram for Boron Isotope Separation in a Polymer System.

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APPENDIX B

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NO.	DATE	REVISION	BY	CHK.

THE GIRDLER CORPORATION
LOUISVILLE, KENTUCKY

SCALE NONE		PROJ. DR. CLG	3/27/53
DRAWN C. A. BAURLE	3-11-53	CHIEF DR.	3/27/53
CHECKED		ENGINEER	3/27/53

FOR: AEC POLYMER PROJECT

867-159
FLOW DIAGRAM
SEPARATION SECTION

DRAWING NO. F-4111-1

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PI - PRESSURE INDICATOR
TI - TEMPERATURE INDICATOR
PRC - PRESSURE RECORDING CONTROLLER
TRC - TEMPERATURE RECORDING CONTROLLER
BPR - BACK PRESSURE REGULATOR
LLC - LIQUID LEVEL CONTROLLER
RO - ROTAMETER
RD - RUPTURE DISC
GG - GAGE GLASS
RV - RELIEF VALVE
DP RC - DIFFERENTIAL PRESSURE RECORDING CONTROLLER

NO.	DATE	REVISION	BY	CHK.

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THE GIRDLER CORPORATION
LOUISVILLE, KENTUCKY

SCALE NONE		PROJ. DR. CLG	3-27-53
DRAWN G.A. BAURLE	3-20-53	CHIEF DR. HCS	3-27-53
CHECKED		ENGINEER J.C.R	3-27-53

FOR: AEC POLYMER PROJECT

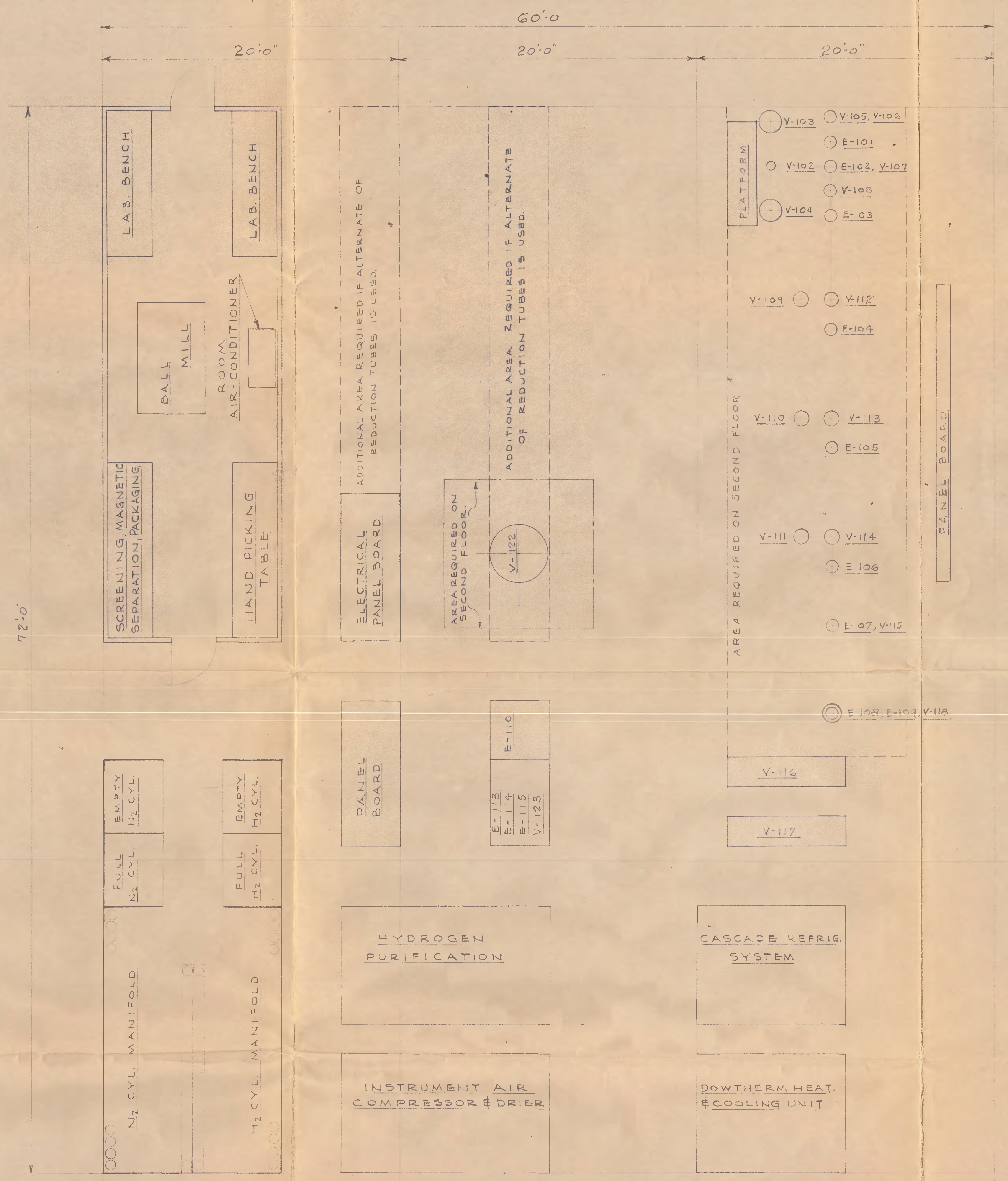
FLOW DIAGRAM
PREPARATION OF
METAL

DRAWING NO. F-4111-2
REV-0

867-160

~~SECRET~~

REFERENCE DRAWINGS & GENERAL NOTES



No.	DATE	REVISION	CO. ORD.	BY	CHK.	ENG.

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By
Date

ISSUED FOR	DATE	DATE	DATE	DATE	DATE	DATE	DATE
PROGRESS							
APPROVAL							
QUOTATION							

THE GIRDLER CORPORATION
LOUISVILLE, KENTUCKY

SCALE ¼" = 1'-0"		DESIGNER CLG	3-27-53
DRAWN C.L. GRAVES C.A. EAURLE	3-24-53	GROUP HEAD HG	3-27-53
CHECKED		ENGINEER J.C.R.	3-27-53

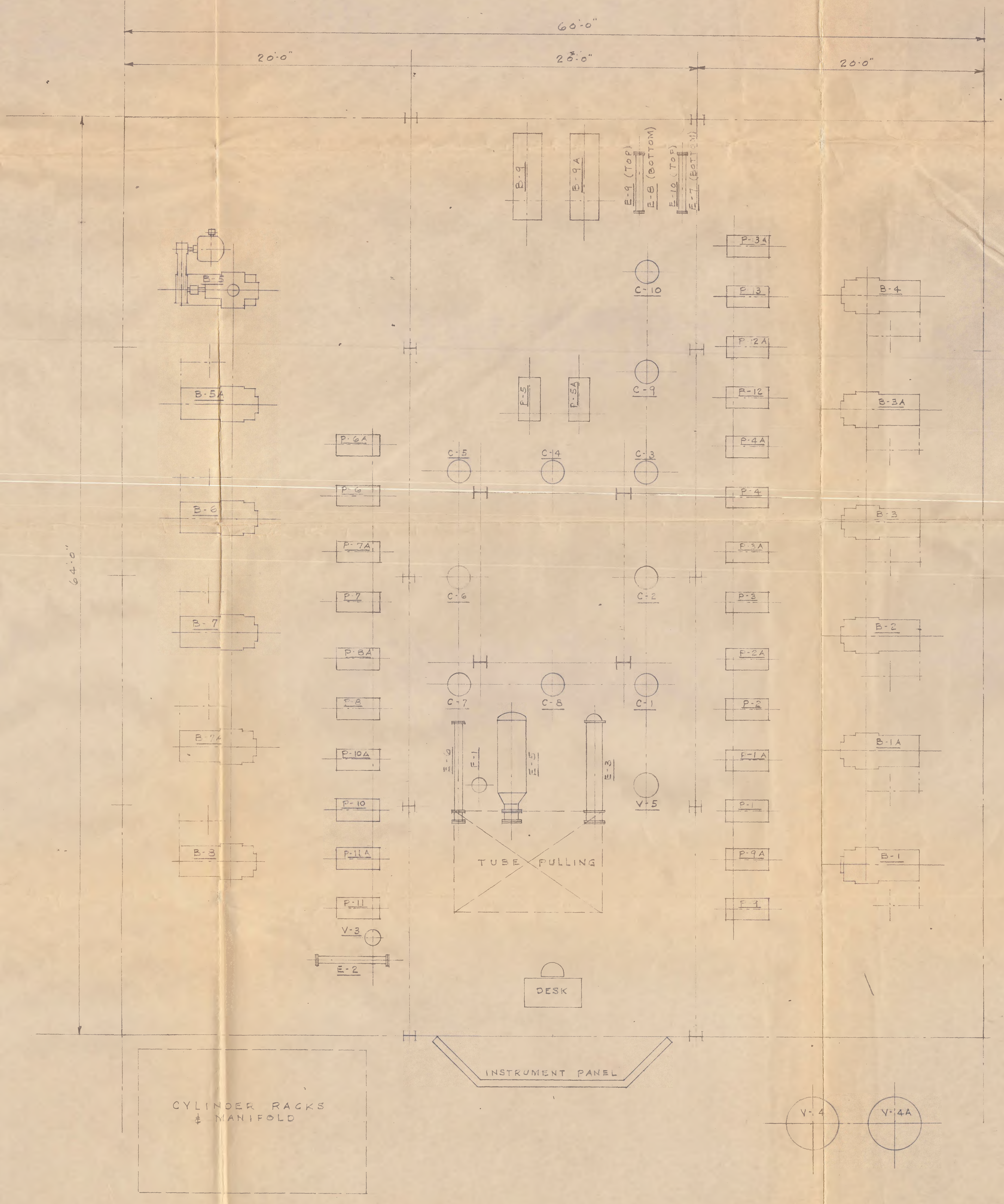
TITLE:
EQUIPMENT LAYOUT
PREPARATION OF METAL

FOR: AEC POLYMER PROJECT

DRAWING NUMBER: E-4111-2
REV.: 0

867-161

867-162



No.	DATE	REVISION	CO-ORD.	BY	CHK.	ENG.

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By

Date

ISSUED FOR	DATE	DATE	DATE	DATE	DATE	DATE	DATE
PROGRESS							
APPROVAL							
QUOTATION							

THE GIRDLER CORPORATION
LOUISVILLE, KENTUCKY

SCALE 1/4" = 1'-0"		DESIGNER C.L.G.	4-2-53
DRAWN C. A. BAURLE	4-1-53	GROUP HEAD	4-2-53
CHECKED		ENGINEER B. J. M	4-1-53

TITLE:

PLOT PLAN
SEPARATION SECTION

FOR:	DRAWING NUMBER	REV.
AEC - POLYMER PROJECT	E-4111-1	0

867-162