Col Peterson
Apr 11-25

0
Summary Report

on

CHLORINATION OF TUBALLOY OXIDES WITH THIONYL CHLORIDE

Submitted

on

February 5, 1946

under

Contract No. W-7405 eng-74

by

Purdue Research Foundation

and

Department of Chemistry, Purdue University

Personnel

Classification changed to Unclassified
Authorized by C.H. Nogg 1-16-56
Changed by Nugli Kihler Date 6-7-12

Advisory and Directing Staff: T. DeVries, Physical Methods; H. B. Hass; H. Hunt and M. G. Mellon, Analytical Chemistry; E. T. McBee, Project Leader; D. W. Pearce, Inorganic Chemistry; and R. N. Shreve, Chemical Engineering.

Research Staff: A. A. Alberts, W. S. Barnhart, R. E. Burns, L. R. Evans, E. S. Gantz, R. E. Hatton, B. W. Hotten, K. W. Krantz, M. Kruder, R. Mezey, J. S. Newcomer, A. M. Ribley, B. F. Rider, G. M. Rothrock, C. V. St. John, R. C. Schreyer, T. S. Taylor, P. E. Weimer, and Z. D. Welch.

Service Staff: J. P. Bennett, B. L. Brown, W. H. Davis, W. E. Fish, C. S. Silverthorn and E. L. VanDermay.

Photostat Price \$ 4.80
Microfilm Price \$ 2.70

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

201 001

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

- 1 - Summary Report

on

Research at Purdue University

by

Purdue Research Foundation and Department of Chemistry

February 5, 1946

CHLORINATION OF TUBALLOY OXIDES WITH THIONYL CHLORIDE

Abstract

1. Tuballoy oxides have been successfully reacted with vapors of thionyl chloride at temperatures in the range of 350-400°C. and at atmospheric pressure to produce tuballoy tetrachloride.
2. This method of producing tuballoy tetrachloride avoids the use of pressures greater than atmospheric, avoids the formation of phosgene and utilizes standard equipment.
3. Ammonium dituballate produces a good grade of tuballoy tetrachloride. Tuballoy trioxide, calcined tuballoy peroxide, trituballoy octoxide, tuballoy peroxide and tuballoy dioxide were also tried and only the tuballoy dioxide failed to produce tuballoy tetrachloride.
4. Temperatures in the range of 350-400°C. were found to be satisfactory and produced the best degree of chlorination.
5. A study of the tuballoy recovery was made. It was found that about 95% of the tuballoy charged was found in the main product and 5% appeared in a sublimate.
6. The nature of the sublimate was not fully investigated. Analysis showed that for each tuballoy atom there were 5.2 atoms of chlorine. The significance of these results is uncertain.
7. Tuballoy tetrachloride was produced by passing vapors of thionyl chloride over tuballoy trioxide contained in a stationary nickel reactor. A suitable scrubbing system removed any tuballoy carried from the reactor by the gases of the reaction. A conversion of about 90% was obtained.
8. The continuous production of tuballoy tetrachloride was investigated. Thionyl chloride was passed countercurrently to the flow of the solid oxide through a rotating nickel tube reactor. Tuballoy tetrachloride was produced at a rate of about one pound per hour. The product for one period of operation contained 62.6% tuballoy, 37.2% chlorine and

201 002

Abstract Cont'd.

1.37% of non-volatile matter. (Theoretical value for tuballoy tetrachloride, 62.6% tuballoy, 37.4% chlorine, 0.0% non-volatile matter.)

9. An internally-stirred reactor was designed and operated. It was hoped that certain losses of tuballoy which escaped at the bearing "ring-seals" of the nickel tube reactor could thus be avoided. A full evaluation of the apparatus was not made.
10. An all-glass reactor which depended upon vibration of the apparatus to move the solid from the feed inlet to the product exit was built and operated. The product obtained was satisfactory but the solid reaction materials had a tendency to cake at regular nodal positions.

201 003

3

CHLORINATION OF TUBALLOY OXIDES WITH THIONYL CHLORIDE

The purpose of research on chlorination of tuballoy oxides was to devise a method for the preparation of tuballoy tetrachloride which would overcome certain objections of liquid-phase chlorination of tuballoy trioxide by carbon tetrachloride. Such a process should include the following features:

1. Production of tuballoy tetrachloride at atmospheric pressure.
2. Complete and rapid conversion of tuballoy oxides to tuballoy tetrachloride, satisfactory for use directly in subsequent steps.
3. Chlorination without the formation of phosgene.
4. Utilization of standard or easily-constructed equipment made of materials not corroded by either reactants or products.

The results of preliminary experiments indicated that chlorination of tuballoy trioxide with thionyl chloride vapors might satisfy the requirements just enumerated. These preliminary investigations were carried out in stationary glass equipment. Experimental conditions, such as the temperature of the reaction and quality of the starting material, and tuballoy recovery were studied. Interpretation of these data led to the construction and operation of equipment for larger size runs in which the characteristics of processes for producing tuballoy tetrachloride continuously or batchwise were compared. The chief objectives of this comparison were the rate and degree of conversion of tuballoy oxides to tuballoy tetrachloride of excellent quality.

Treatment of Tuballoy Oxides with Vapors of Thionyl

Chloride in Stationary Reactors

Equipment and Preliminary Experiments. Chlorination of Tuballoy trioxide to tuballoy tetrachloride with thionyl chloride (Paragon Testing Laboratory) was accomplished by passing thionyl chloride vapors, formed by dropwise addition of liquid thionyl chloride into a hot combustion tube, over the tuballoy trioxide maintained at a temperature of about 350°C.

The apparatus consisted of a Pyrex combustion tube, 25 mm. in diameter and about 100 cm. long, which served as the main reaction chamber. It was placed horizontally in an electric tube-furnace. Thionyl chloride was introduced into one end of the tube from a dropping funnel. The exit gases were passed through a suitable water scrubber before being vented. The sample of the tuballoy trioxide contained in a porcelain boat was placed in the center of the reaction tube. Temperature measurements were made by means of a chromel-alumel thermocouple inserted in a glass well near the center of the combustion tube.

201 004

In a preliminary experiment, thionyl chloride vapors were passed over tuballoy trioxide at a temperature of about 475°C. The color of the sample changed quickly from a bright orange to a dark brown. A yellow sublimate condensed on the cool portions of the reaction tube and brown fumes were observed arising from the material in the boat. After thionyl chloride vapors were passed over the oxide sample for one hour, the thionyl chloride feed was stopped and the tube allowed to cool to room temperature. The product, still in the reaction tube, appeared to have a reddish brown metallic luster. Upon exposure to air, this material immediately turned green. The product contained 35.4% chlorine (theoretical chlorine content of tuballoy tetrachloride is 37.6%) and was completely soluble in water.

Study of Reaction Time. A portion of tuballoy trioxide was treated with thionyl chloride vapors in the apparatus just described, the purpose being to study the effect produced by varying the time of exposure. Therefore, a sample of the product was removed at the end of one-half hour and another at the end of one hour. These samples were analyzed. The results obtained are summarized as follows:

Reaction Time, hr.	Temperature Range, °C.	Chlorine Analysis, %
0.5	317-400	36.8
1	317-407	36.8

It is evident from these data that a good grade of tuballoy tetrachloride was produced in about one-half hour and that subsequent exposure to thionyl chloride did not increase the chlorine content of the product.

Study of Reaction Temperature. Two samples of tuballoy trioxide were treated with vapors of thionyl chloride at different temperatures for one hour. The data obtained are as follows:

Sample	Reaction Time, hr.	Temperature Range, °C.	Chlorine Analysis, %
A	1	195-218	34.9
B	1	317-407	36.8

The product obtained from sample A was bright green when exposed to air and lighter in color than the product obtained from B. It is evident from these data that the conversion of tuballoy trioxide to tuballoy tetrachloride was more nearly complete at the higher temperature range.

Comparison of the Behavior of Different Tuballoy Oxides with Thionyl Chloride. Various tuballoy oxides were treated with thionyl chloride vapors and the characteristics of the final products compared.

a. Calcined tuballoy peroxide. A quantity of tuballoy trioxide was prepared by treating a buffered tubanyl chloride solution with hydrogen peroxide, removing the yellow precipitate by filtration, drying the peroxide

cake at 110°C.; and finally calcining the cake at 300°C. in a slow current of dry air.

A sample of the tuballoy trioxide thus prepared was treated with vapors of thionyl chloride at 317-307°C. for one hour. The product was dark green in color, very deliquescent, and had a chlorine content of 36.8%.

b. Calcined ammonium dituballate. Ammonium dituballate was prepared in the following manner: A tubanyl nitrate solution was prepared by dissolving tuballoy trioxide (Mallinckrodt purified) in an excess of nitric acid. Ammonium hydroxide was added to the tubanyl nitrate solution until precipitation was complete. The yellow precipitate was removed by filtration, calcined in a stream of dry air at 350°C., and then treated with thionyl chloride vapors at 340-368°C. for one hour. The product appeared similar to that obtained from calcined tuballoy peroxide and contained 36.5% chlorine.

c. Trituballoy octoxide. A sample of tuballoy trioxide (obtained by calcining tuballoy peroxide) was heated in a muffle furnace at 790-850°C. for 2.5 hours. The uniform dark gray product was assumed to be essentially trituballoy octoxide. This material was treated with vapors of thionyl chloride at 338-374°C. for one hour. Analysis of the product showed it to contain 33.6% chlorine. The conversion of trituballoy octoxide to tuballoy tetrachloride was not as complete as in the case of the reaction of tuballoy trioxide with thionyl chloride under similar conditions.

d. Tuballoy peroxide. A porcelain boat containing tuballoy peroxide, dried at 110°C. and pulverized, was placed in the reaction tube already heated to 349-358°C. and thionyl chloride vapors passed over the oxide for one hour. The product from visual observation appeared to be identical with that obtained from tuballoy trioxide. It contained 35.5% chlorine.

e. Tuballoy dioxide. A sample of tuballoy dioxide (Mallinckrodt) was treated with thionyl chloride at about 350°C. The product was a firmly-caked black solid, partially soluble in water; it contained 1.7% chlorine. The results indicate that little, if any, tuballoy tetrachloride was formed.

f. Mallinckrodt tuballoy trioxide. Mallinckrodt purified tuballoy trioxide when treated with vapors of thionyl chloride at about 350°C. gave a very hard sintered product. Unreacted yellow particles (presumably tuballoy trioxide) were visible upon examination of a cross section of the product.

In an effort to determine the cause of the sintering, several experiments were performed. A sample of Mallinckrodt purified tuballoy trioxide was passed through an 80-mesh sieve and the fines obtained were treated with vapors of thionyl chloride at about 350°C. Sintering occurred. On the other hand, a sample of these fines did not sinter when heated at 350°C. for one hour in the absence of thionyl chloride. In another experiment, a portion of unscreened tuballoy trioxide was converted to trituballoy octoxide by heating to 800°C.; no sintering occurred. However, upon treatment of this trituballoy octoxide with vapors of thionyl chloride, a hard sintered product was produced. Next, a sample of tubanyl nitrate hexahydrate

(Mallinckrodt) was heated to a temperature of 363°C. After 40 minutes, evolution of oxides of nitrogen had ceased and conversion to tuballoy trioxide appeared to be complete. Vapors of thionyl chloride were then passed over this tuballoy trioxide for 30 minutes at temperatures in the range of 350-400°C. The product obtained was loose and flaky with no indication of its being sintered; it had the normal appearance of tuballoy tetrachloride made from thionyl chloride and calcined tuballoy peroxide. The cause of the sintering was not determined by these experiments.

Study of Tuballoy Recovery. Several attempts were made to obtain a complete tuballoy recovery following the reaction between thionyl chloride and tuballoy trioxide. The starting material chosen for this investigation was calcined ammonium dituballate.

In a typical experiment, a sample of calcined ammonium dituballate was weighed and treated with vapors of thionyl chloride in a temperature range of 345-358°C. for one hour. At the end of this time, the apparatus was swept with a slow stream of dry nitrogen for one hour in order to remove excess thionyl chloride. The main product which was in the porcelain boat was dissolved in water. No insoluble residue was observed in the solution. The final volume was adjusted to exactly 500 ml. in a volumetric flask and an aliquot of the resulting solution was taken for a tuballoy determination.

During this reaction some material sublimed and condensed in the relatively cool zones of the reactor. This material was washed from the reactor with water, sulfuric acid was added and the whole was evaporated to fumes of sulfur trioxide. The total amount of tuballoy was then determined. The data and results are summarized as follows:

Tuballoy charged, ml. (a)	594.8
Tuballoy recovered, ml. (a)	
in the main product	565.4
in the sublimate	34.4
Total tuballoy recovered, ml. (a)	599.8
Tuballoy recovery, %	100.8

(a) Tuballoy content is given in terms of ml. of standard $K_2Cr_2O_7$ solution.

Thus 100.8% of the tuballoy charged was recovered with about 95% as the main product and 5% as sublimate.

Study of the Nature and Quantity of Sublimate. The sublimate obtained from the thionyl chloride reactions varied in nature from a crystalline reddish-brown solid to an amorphous lemon-yellow powder. In many cases, a trace of green color could be detected among the other colors. The fact that the sublimate was soluble in water led to the belief that it consisted of tuballoy compounds. The heterogeneity of colors indicated that the sublimate may have

consisted of a mixture of tubanyl chloride, tuballoy tetrachloride, tuballoy pentachloride and tuballoy hexachloride; some of these compounds have high vapor pressures. In one experiment, the ratio of chlorine to tuballoy in the sublimate was determined by preparing an aqueous solution of the sublimate from a typical reaction and analyzing aliquot parts. The ratio obtained was 5.2 atoms of chlorine per atom of tuballoy. This ratio may indicate that the sublimate consisted essentially of tuballoy pentachloride. The significance of the results of the analysis, however, is uncertain. It is difficult for one to understand how a sublimate, the major portion of which in most cases appeared to be a yellow powder, could consist of tuballoy pentachloride. A more plausible interpretation of these data is that the sublimate consisted of a mixture of tuballoy chlorides including oxychlorides.

Tuballoy Conversion and Recovery. Data from experiments previously mentioned in this report showed that about 95% of the tuballoy charged into the reactor was recovered as tuballoy tetrachloride and 5% of the tuballoy was recovered in the sublimate. The green coloration of the sublimate may be evidence for the existence of tuballoy tetrachloride in the sublimate. No satisfactory method for determining the proportions of the constituents in the sublimate was available and time did not permit a conclusive study of analytical procedures.

Large Scale Production of Tuballoy Tetrachloride. Based upon the results of the preliminary experiments, calcined ammonium dituballate was chosen as the starting material for a large scale production of tuballoy tetrachloride.

Corrosion tests with nickel and steel in the presence of tuballoy trioxide and thionyl chloride at 300-360°C., proved nickel superior to steel. Hence nickel was chosen as a material of construction for the reactor.

The nickel reactor consisted of a rectangular box, eight inches by four inches by sixty inches containing two trays of sheet nickel, each six inches wide, fifty-five inches long and one inch deep. The upper tray was supported by legs which rested on the lower tray. A thermocouple well extended full length through the center of the reactor between the trays. Nickel pipe welded to each end of the reactor served as the reactor inlet and exit. The feeding apparatus consisted of a large separatory funnel which served as a thionyl chloride reservoir, and a tube connecting the funnel to the reactor inlet. Feed rate was regulated by adjustment of the stopcock of the funnel. The reactor was placed in a rectangular electrical heater. A five-inch clearance between the end walls of the reactor and the ends of the trays prevented channeling of thionyl chloride vapors which were formed when liquid thionyl chloride came in contact with the hot end walls of the reactor.

The scrubber system consisted of a trap to catch any condensed thionyl chloride, a tower packed with glass helices, a water wash-bottle and a sulfur dioxide scrubber.

For the preparation of tuballoy tetrachloride using the nickel reactor and trapping system just described, a charge of 3290 g. of 40 mesh calcined ammonium dituballate was treated with 5450 g. of thionyl chloride

for 20 hours. The thionyl chloride feed was fairly regular except when occasional plugging of the reactor outlet necessitated the discontinuance of the feed.

Temperatures were measured by means of thermocouples placed at three points in the reactor, namely, ten inches from the exit end, at the center, and ten inches from the feed or inlet end of the reactor. These points were designated as L, M and S, respectively. The following temperature ranges were maintained throughout the entire reaction period:

L	350-94°C.
M	350-96°C.
S	287-303°C.

At the end of the reaction period, there was removed from the trays 4035 g. of product which appeared as a green, microcrystalline powder. The product was transferred while hot to air-tight storage bottles. A sample of well-mixed product was found to contain 36.0% chlorine and 61.3% tuballoy for a chlorine to tuballoy ratio of 3.95.

A variegated green sublimate was washed from the walls of the reactor with water. The resulting solution contained 149.9 g. of tuballoy.

The scrubbing system contained 137.6 g. of tuballoy. If it is assumed that the original charge was pure tuballoy trioxide, the following calculations apply:

<u>Source of Tuballoy</u>	<u>Tuballoy Recovery, %</u>
Tuballoy Tetrachloride	90.5
Condensate from reactor walls	5.5
Sublimate and scrubbing system	5.0
Total	101.0

These data show that the tuballoy tetrachloride produced was of good quality, with a conversion of about 90.5%. And as in the preliminary experiments, about 5% of the tuballoy charged was recovered in the sublimate and scrubber system.

Summary. Tuballoy trioxide may be chlorinated with thionyl chloride in the vapor phase at a temperature of about 350°C. and with a contact time of one-half to one hour. Satisfactory tuballoy tetrachloride may be produced from either calcined ammonium dituballate, tuballoy peroxide, or calcined tuballoy peroxide. Of the various tuballoy oxides available, tuballoy dioxide gave the poorest grade of tuballoy tetrachloride. Mallinckrodt purified tuballoy trioxide produced a hard sintered product.

A tuballoy recovery of 100.8% was obtained in a study of the reaction between calcined ammonium dituballate and vapors of thionyl chloride. Similar studies showed that about 5% of the tuballoy charged appeared in a sublimate. The exact nature of the compounds in the sublimate was not determined.

In a large scale experiment, calcined ammonium dituballate was treated with vapors of thionyl chloride in a nickel reactor. A conversion of about 90% of satisfactory tuballoy tetrachloride was obtained. About 5% of the tuballoy charged was found in the sublimate and scrubber wash solutions.

Continuous Production of Tuballoy Tetrachloride

Since tuballoy tetrachloride of good quality may be prepared by the vapor phase reaction of thionyl chloride and tuballoy trioxide, several devices for the continuous production of tuballoy tetrachloride were designed and operated. The main objectives of this study were the continuous production of high grade tuballoy tetrachloride and an excellent as well as a rapid conversion of tuballoy trioxide to tuballoy tetrachloride.

Rotating Reactor. Nickel was again chosen as the material of construction because of its high resistance to corrosion by the reactants and resultant products of chlorination of tuballoy trioxide by thionyl chloride at temperatures of 350-400°C. The reactor consisted of an electrically heated nickel tube, 5 feet long and 4 inches in diameter, elevated at an angle about 10 degrees from the horizontal, and rotated by a chain drive (13) at a speed of about 2 r.p.m. The details of the reactor are shown in Figure 1.

Tuballoy trioxide was placed in the hopper (15) and was transferred into the reactor (9) by the screw feed (18). The screw was turned by a pulley arrangement at a speed of about 5 r.p.m. To aid the delivery of tuballoy trioxide into the tube, a Syntren vibrator (12) was belted to the hopper. A 6 foot nickel rod (17), placed in the rotating tube, helped to mix the solid. The solid reaction products, by gravity and tube rotation, moved to the lower end where they were delivered into a heated bottle (2) which could be changed readily. The rotating tube was heated by four Hevi-Duty furnaces (8). Temperature measurements were made by means of Iron-Constantan thermocouples attached to a recording Micromax potentiometer. The thermocouples were inserted in a well (4) made of nickel. Liquid thionyl chloride was delivered into the preheater (1) where it vaporized before passing counter-currently over the solid in the reactor.

The trapping system consisted of two flasks (19, 21) used as dust collectors and a packed scrubbing tower (22) backed by an auxiliary water scrubber (25). The exit gases and dust passed through the exit pipe (14), into the first flask. Most of the dust collected at this point. A continuous stream of water passing through the scrubbing tower removed the tuballoy that passed through the first trap. Volatile products that escaped these traps were thoroughly scrubbed by the final water trap before being allowed to escape. The pressure in the whole system was reduced slightly by means of a water aspirator attached to the final outlet of the

trapping system. The purpose of reducing the pressure was to prevent gases containing volatile tuballoy compounds from escaping into the atmosphere through the graphite ring bearing (3, 2) surfaces of the reactor unit. The general operating procedure of the rotating-tube reactor, as will be described, was followed throughout these experiments.

The reaction tube, rotating at 2 r.p.m., was heated to a temperature in the range of 350-400°C. Liquid thionyl chloride was added dropwise at a suitable rate into the vaporizer and the pressure was slightly reduced in the system. When vapors of thionyl chloride entered the scrubbing tower, a charge of tuballoy trioxide was placed in the hopper and the feed screw started. Data for a period of operation from Experiments P-5C and P-6C, in which the best chlorinated product from tuballoy trioxide was obtained, are given in Table 1. In Experiment P-5C, 118 g. of a tan colored dust was collected in the first trap and found to contain 26% chlorine. In the other parts of the scrubbing system, 31.5 g. of tuballoy was found which is equivalent to 2.2% of the amount of tuballoy originally charged into the reactor. The tuballoy tetrachloride containing 34.0% chlorine was of poor quality.

At the end of Experiment P-6C the reactor tube was found to be clogged with a hard, dense, sintered material. The product obtained was unsatisfactory.

In another experiment, P-16C, calcined ammonium dituballate was chlorinated. The starting material was prepared as follows. A quantity of Mallinckrodt purified tuballoy trioxide was dissolved in hydrochloric acid and the solution made alkaline with an aqueous solution of ammonia. The resultant precipitate was filtered, washed, dried and finally calcined at 300°C. for about 8 hours. The calcined product was ground until it passed through a 16-mesh sieve. In general, the operating procedure followed the plan used in previously described chlorinations with thionyl chloride. This experiment was run continuously for about 15 hours. The data for two time intervals during this experiment are given in Table 2.

It is made evident by a comparison of the data presented in Table 1 with those in Table 2 that, of the various possible starting materials, calcined ammonium dituballate produced the best grade of tuballoy tetrachloride in the rotating-tube reactor. In view of this, subsequent experiments were conducted using calcined ammonium dituballate prepared as previously described.

An experiment, RM-3, was performed in which an attempt was made to produce over a long period of time a consistently good product by chlorinating calcined ammonium dituballate with thionyl chloride in the rotating-tube reactor.

Ammonium dituballate was prepared from Mallinckrodt purified tuballoy trioxide. Calcination was carried out at 280-360°C. About 38 pounds of material was prepared for use in Experiment RM-3 and was found to contain 1.83% of chlorine, 80.4% of tuballoy with traces of magnesium, silicon, copper and nickel.

Table 1

Chlorination of Tuballoy Trioxide with Thionyl Chloride

Expt. No.	P-5C	P-6C
Rotation rate, r.p.m.		
feed screw	5	5
reactor tube	2	2
Contact time, hrs.	4.2	4.2
Tuballoy trioxide,		
identification	723	264
size, mesh	16	--
apparent density, g./cc.	1.45	4.04
total amount fed, lb.	4.13	13.8
rate of feed, lb./hr.	1	3.3
Thionyl chloride,		
total amount fed, lb.	6.12	5.9
rate of feed, lb./hr.	1.5	1.4
Temperature, °C.		
1. feed end, TO_3	370-440	409
2. center	356-390	
3. center	377-410	
4. exit end, TCI_4	347-385	348
Analysis of product, %		
chlorine	34.0	20.2

Table 2

Chlorination of Ammonium Dituballate with Thionyl Chloride

Expt. No.	Period A P-16C	Period B P-16C
Time, hr.	1:20	4:15
Calcined ammonium dituballate,		
total feed, g.	450	264
feed rate, g./hr.	337	62
feed rate, lb./hr.	0.75	0.14
analysis: tuballoy, %	79.4	79.4
Thionyl chloride (Hooker)		
total feed, g.	544	2315
feed rate, g./hr.	408	543
feed rate, lb./hr.	0.90	1.20
Temperatures, °C.,		
1. inlet, feed end	344-398	322-406
2. right center	342-400	292-382
3. left center	---	335-396
4. exit, product end	342-406	292-382
Weight of product, g.	311	500
Analysis of product, %		
chlorine	36.3	36.9
tuballoy	---	62.7

Over a period of 34.3 hours, 15.97 kg. of thionyl chloride was allowed to react with a charge consisting of 14.65 kg. of calcined ammonium dituballate. The amount of product obtained was 11.77 kg. From these data it was calculated that the rate at which calcined ammonium dituballate entered the reactor was 0.94 pounds per hour, the thionyl chloride rate was 1.02 pounds per hour and the delivery rate of the product was 0.75 pounds per hour. Variations in temperature for various parts of the reactor were also observed but all temperatures during the course of the experiment were between 300 and 400°C. The analytical results for various fractions of the product are given in Table 3.

Upon completion of the run, the reactor was disassembled and carefully examined. A considerable amount of tuballoy-containing substances was found adhering to the interior wall of the reactor tube, especially at the point where the feed screw ended. Lesser amounts were found on the thermocouple well and on the inside of the syphon bellows (5 in Figure 1),

It is evident that a good quality of tuballoy tetrachloride can be produced from tuballoy oxides and thionyl chloride in the rotating-tube reactor. The following data taken from Table 3 indicate the quality of the best tuballoy tetrachloride produced:

Tuballoy tetrachloride	<u>Tuballoy, %</u>	<u>Chlorine, %</u>	<u>Ratio, Cl/T</u>	<u>Non-volatile Matter, %</u>
Sample RM-3J	62.6	37.2	3.99	1.37
Theoretical value	62.6	37.4	4.00	0.00

It should be pointed out, however, that material having a quality as high as obtained in Sample RM-3J was not produced during the major portion of any continuous run. The total quantity of high-quality material in the 34 hour run (RM-3) was about 2.5 pounds. The inconsistency in quality of the product can be ascribed to several varying conditions during the experiment. The solid feed rate varied from 690 g./hr. to 40 g./hr.; the temperature varied considerably in many instances and for no apparent reason. On the other hand, the thionyl chloride feed rate was relatively uniform. If the reaction can be represented by the equation,

much less than the theoretical quantity of thionyl chloride was used in many of the time intervals. Each sample taken (see Table 3) represents approximately the same time interval. Thus it becomes evident, that the ratio of tuballoy trioxide to thionyl chloride must also be considered in ascertaining the cause of the variable results observed.

The results of the experiment show that production of tuballoy tetrachloride in excess of three pounds per hour was not practical with the existing equipment. The best product obtained was produced at a rate of less than one pound per hour.

Table 3

Analyses of Products from Experiment RM-3

<u>Sample</u>	<u>T, %</u>	<u>Cl, %</u>
RM-3A	63.9	29.5
RM-3B	64.7	30.6
RM-3C	66.4	28.4
RM-3D	65.5	31.2
RM-3E	65.6	29.0
RM-3F	65.0	30.4
RM-3G	63.2	37.8
RM-3H	63.8	36.6
RM-3J	62.6	37.2
RM-3K	64.4	32.6

Figure 2

Internally Stirred Reactor. In the search of an efficient reactor for producing tuballoy tetrachloride continuously by the reaction of vapors of thionyl chloride and tuballoy trioxide, a stationary horizontal nickel tube reactor, internally stirred, was designed.

The reactor consisted of a stationary horizontally-arranged nickel tube, 6 feet long and 4 inches in diameter. The stirrer blades were attached to a central shaft and were pitched so as to force the solid toward the delivery end of the reactor upon rotation of the stirrer. Clearance between the walls of the tube and the ends of the stirrer blades was about 0.25 inch.

Tuballoy trioxide at room temperature was introduced into this reactor through a rotating tube of nickel (6 feet long, 4 inches in diameter) into which the tuballoy oxide charge was led from a hopper. The internally stirred reactor was maintained at a temperature of about 350°C. As with the rotating-tube reactor, vapors of thionyl chloride moved counter-currently to the solid flow. Thionyl chloride vapors entered the reactor at the product-delivery end, passing first through the reactor, then through the rotating tube and finally into a scrubbing system from which the tuballoy-free reaction gases escaped.

The purpose of this arrangement was an attempt to entrain and collect the sublimate and dusts, which are normally formed in the hot reaction tube, with the incoming charge in the relatively cool rotating tube. Thus, these entrained materials would be repassed through the hot reaction zone; the output of tuballoy tetrachloride should have been increased by this arrangement.

After continuous addition of tuballoy trioxide for a period of five to six hours, virtually no product had been obtained. This was probably due to the large hold-up in the internally stirred reactor.

No subsequent experiments were carried out with this equipment because of the limitation of time.

Vibrating Glass Reactor. One proposal made to overcome the difficulties encountered in the previous work was to agitate and propel the solid through a reactor by vibration. To this end, a Syntron vibrator was attached to a heater rack supporting a glass tube reactor. One end of the reactor was elevated so that the solid material upon vibration traveled to the lower end where it was collected in a heated receiver. The apparent advantage of this method was that there were no moving parts through which reaction gases and sublimate could escape.

The final arrangement of the equipment is shown in Figure 2. The reaction chamber was a section of 28 mm. Pyrex tubing, 120 cm. long. Solid tuballoy trioxide was placed in the reservoir (1) from which it passed through the reservoir stem and dropped into the horizontal section of the reactor (4). The vibration and the downward slant of the reactor tube caused the solid to move towards the exit. A slow stream of nitrogen introduced through the feed tube side arm (3) prevented the reaction gases from entering the feed tube (2). The rate of flow of the solid was controlled by changing the distance between

the end of the stem of the reservoir and the reaction chamber or by changing the amplitude of vibration.

Inasmuch as a Syntron vibrator (11) could not readily be attached to the glass reactor without danger of shattering the glass tube, the Syntron vibrator was bolted to the heater rack (12) to which the glass tube was also clamped (14). Thus this danger was overcome. Yet the transmittance of the vibration was not seriously hampered. The heaters (7) were Hevi-duty furnaces and were arranged so that no part of the heaters could come into direct contact with the glass reactor tube. The receiver (5) was electrically heated by a resistance tube heater (6) in order to prevent contamination of the product with condensed vapors of thionyl chloride.

The thionyl chloride vaporizer consisted of a flask heated by a hot plate and connected to the reactor by means of a hemispherical ground glass joint (8). The entire thionyl chloride feeding apparatus was made of glass as was the scrubbing system which was attached to the other end (13) of the reactor.

Several preliminary experiments of a qualitative nature were conducted using both Mallinckrodt tuballoy trioxide and calcined ammonium dituballate. It was observed that Mallinckrodt tuballoy trioxide fed more rapidly than the calcined ammonium dituballate. This undoubtedly was due to the higher apparent density of the Mallinckrodt material.

The general procedure for the operation of the vibrating reactor was as follows:

The reservoir was filled to capacity with a sample of tuballoy trioxide. Nitrogen was passed slowly through the nitrogen inlet tube. Vapors of thionyl chloride were passed through the system and the Syntron vibrator adjusted until the amplitude of vibration caused the granular solid to flow through the reactor at the desired rate. The tuballoy tetrachloride was discharged into a heated collector bottle. The reaction gases were passed through a suitable scrubbing system, similar to that used with the stationary glass reactor already described, and then allowed to escape.

Various characteristics of the operation, namely, the tendency of the materials to cake, movement of the solid, and the solid feed mechanism, were important factors in determining the practicability of the vibrating reactor.

It was noticed that whenever any reacted or partially reacted solid collected at a point where thionyl chloride vapors could condense, caking of the solid occurred. The greatest amount of caking occurred when Mallinckrodt tuballoy trioxide was used. Consequently, in the final arrangement of the apparatus, the number of cool areas in which thionyl chloride vapors could condense were reduced to a minimum. However, even with this arrangement, caking was observed.

The movement of the solid was next considered. The solid did not flow at a steady rate toward the discharge end of the reactor. Certain nodes

appeared in the tube which held up the uniform flow of solid material. Very little control over the presence or position of these nodes could be maintained. Furthermore, the nodes changed their positions during the operation even though there was no change in the amplitude of vibration or in the position of the apparatus. Caking was always prominent at the node positions. Agitation of the solid by vibration appeared to be sufficient to give good contact with vapors of thionyl chloride, but apparently insufficient to prevent caking.

The solid feed mechanism was of the gravity type as shown in Figure 2 and proved to be satisfactory. It was found that when nitrogen was not passed into the feeding mechanism, the end of the reservoir exit became plugged after a few minutes of operation. This may have been caused by a reaction between fresh tuballoy trioxide and thionyl chloride which entered the inlet tube from the reactor. (This phenomenon may explain the large variations in feed rate found in the rotating reactor.) No such difficulty was encountered whenever nitrogen was passed slowly into the inlet tube.

It was found that the quality of the product depended, for the most part, upon the length of time that vapors of thionyl chloride were in contact with tuballoy trioxide. It was noted that whenever the solid was sent rapidly through the reactor, conversion was always poor. The exposure time could be increased by decreasing the tilt of the reaction tube but, whenever this was done, there was an increased tendency for the solid to pile-up at the node positions. It was further observed that in these instances where good conversions had taken place, caking was also prevalent.

Summary. A rotating reactor was built and operated for the purpose of producing tuballoy tetrachloride continuously at a rate of about one pound per hour by the chlorination of tuballoy trioxide with vapors of thionyl chloride. Calcined ammonium dituballate gave a tuballoy tetrachloride product which was of better quality than that produced from Mallinckrodt purified tuballoy trioxide. The major part of the product obtained during a 34 hour continuous operation period consisted of about 93% tuballoy tetrachloride.

An internally stirred reactor was built and operated in conjunction with the rotating reactor. Definite conclusions could not be drawn inasmuch as insufficient data were obtained because of time limitation.

A vibrating glass reactor was constructed and operated. The feeding device for the solid material was found to be very satisfactory. However, the tendency for the solid materials to cake in the reaction chamber became a serious problem in the successful operation of this reactor.

Respectfully submitted,

E. T. McBee

E. T. McBee
Project Leader

D. W. Pearce

D. W. Pearce

R. Mezey

R. Mezey

0-20