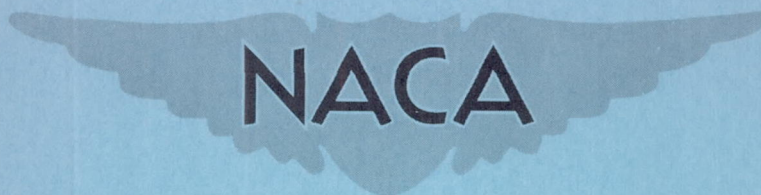


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RESEARCH MEMORANDUM

THE SYNTHESIS OF BUTYLSILANES BY A LARGE-SCALE REDUCTION
WITH LITHIUM ALUMINUM HYDRIDE

By Samuel Kaye, Stanley Tannenbaum
and Harold F. Hipsher

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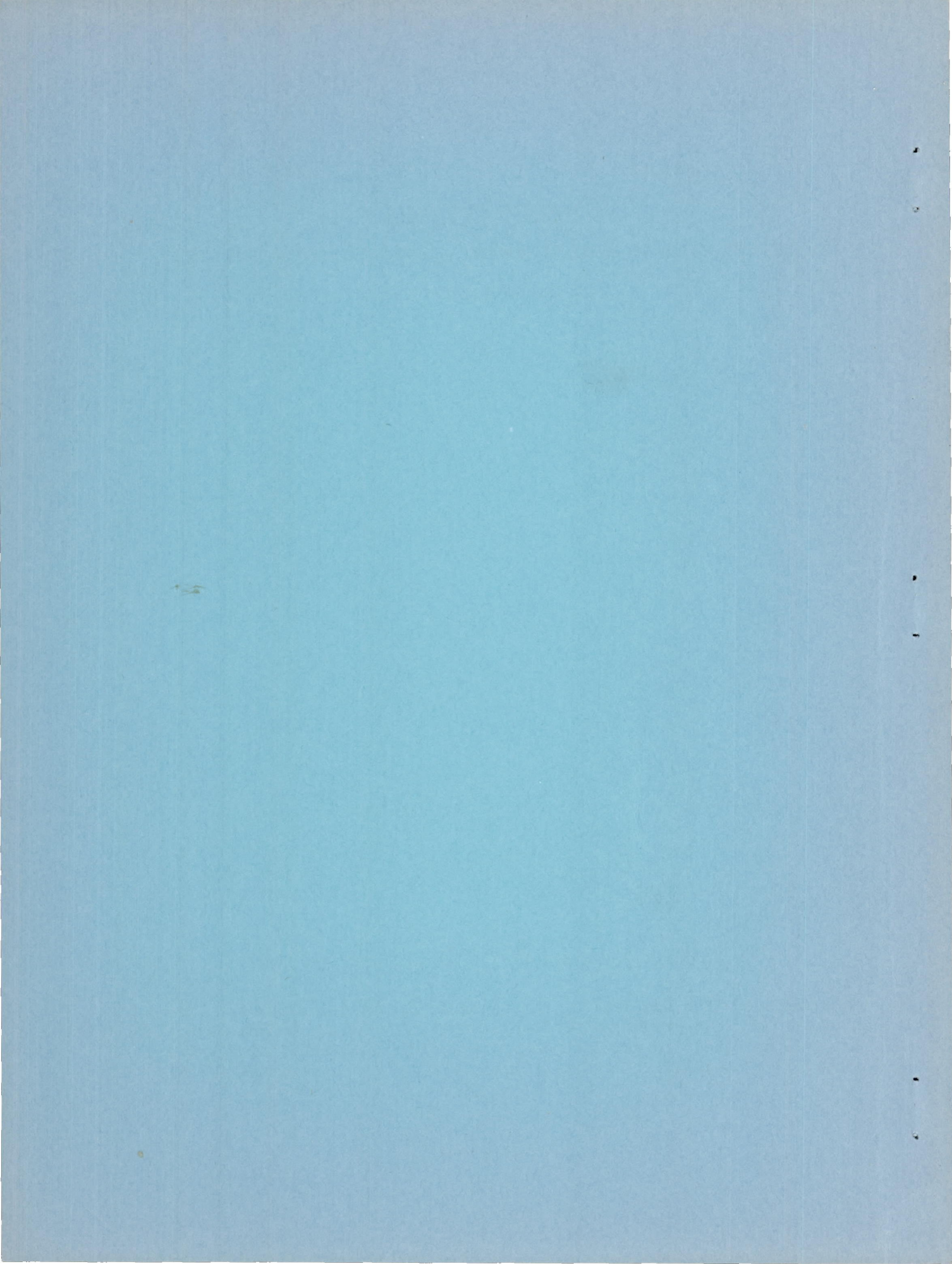
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LITHIUM ALUMINUM HYDRIDE

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SUMMARY

Eighty pounds of butylsilanes required for test purposes was synthesized by reducing butyltrichlorosilane with lithium aluminum hydride in dioxane solution. This was safely and successfully accomplished by operating in steel equipment under an atmosphere of oil-pumped nitrogen to minimize the hazards involved in conducting this operation on a large scale. The apparatus and procedure used to carry out the necessary manipulations are described in this report.

INTRODUCTION

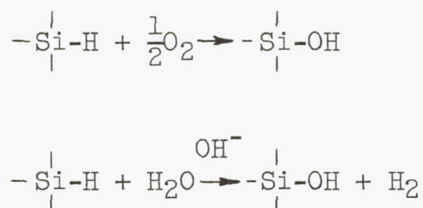
As part of a series of investigations at the NACA Lewis laboratory on flame speeds, ignition, and other burning characteristics of high-energy fuels, several alkylsilanes were prepared in laboratory quantities and their chemical and physical properties reported (ref. 1). The results of preliminary combustion studies suggested that further studies in a large-scale combustor might yield information useful for the evaluation of these compounds as fuels or fuel components for jet aircraft. This necessitated the preparation of large quantities of butylsilanes.

Although these compounds had been prepared previously on a small scale (ref. 2), no information was available on any large-scale preparation. The laboratory synthesis reported previously proceeds according to the reaction



The same reaction was used in the research reported herein, but the scale-up of this synthesis to the quantity of product desired magnified several difficulties and hazards associated with this reaction and required a careful refinement of technique, which is reported in this paper.

The finely ground lithium aluminum hydride required for the synthesis is subject to deterioration by reaction with oxygen and moisture in the atmosphere. Under some conditions it is pyrophoric in air. A second difficulty was introduced by the possible toxicity of butyltrichlorosilane and its ease of hydrolysis in moist air to evolve acid fumes. Finally, the products, butylsilanes, are themselves reducing agents and could be oxidized by air, especially at elevated temperatures, or by water in the presence of hydroxyl ion (ref. 3, p. 6):



These problems were solved by covering materials in the reactor with an inert atmosphere of nitrogen and by manipulating lithium aluminum hydride and making necessary transfers of material in systems sealed from the atmosphere. The techniques used for the manipulations are described. The largest single batch of product prepared yielded an estimated 27 pounds of mixed butylsilanes.

APPARATUS

Preliminary experiments were run in the 5-gallon reactor shown in figure 1, but the main portions of the product were prepared in the 50-gallon reactor (fig. 2(a)). A diagram showing the layout for the 50-gallon reactor is shown in figure 2(b). The small reactor was made of stainless steel and was jacketed for steam or hot or cold water. The dished top was fitted with a stainless-steel stirrer and baffle plate. Solvents and butyltrichlorosilanes were added to the reactor by gravity from a double-valved addition tank provided with a nitrogen purge line. The rate of addition could be determined visually by means of a sight glass between the tank and the reactor.

The tank for the addition of lithium aluminum hydride slurry was placed on a fitting between the reactor and the glass-lined reflux condenser attached to the reactor. This tank was double-valved, made of Inconel, and provided with a fitting for blanketing the slurry with nitrogen. To avoid plugged openings due to caking, gate valves were used. If plugging did occur, pressurized nitrogen sufficed to force the slurry through the large opening. A sight valve below the condenser afforded a means for checking the rate of reflux. Additional information on the course of the reaction was obtained from three thermocouple

stations located in the water jacket, in the reactor next to the stirrer, and in the condenser reflux line. Atmospheric air and moisture were kept out of the system by means of a check valve in the condenser vent. For safety purposes, the spent residues from the reaction were discharged through a double-valved line into a portable container which was likewise fitted with a nitrogen purge line. The product receivers were double-valved $4\frac{1}{3}$ -gallon tanks fitted with a nitrogen inlet and outlet.

The 50-gallon reactor was constructed similarly except for the following details. The butyltrichlorosilane was fed by gravity into a nitrogen purged reservoir tank fitted with a sight gage and a sight glass. The solvents for the reaction were pumped directly from a 55-gallon drum into the reactor by a rotary pump through a T-fitting which held a nitrogen purge line.

The powder-addition tank used to add lithium aluminum hydride to the large reactor is shown in figure 3. It consisted of a stainless-steel tank to which the nut of a $2\frac{1}{2}$ -inch union was welded. The face of the pear-shaped valve was spherically ground to close on the seat of the pipe union. The valve was manipulated by means of a rod which extended through the container and was sealed from the outside atmosphere by an O-ring. Several scrapers were welded to the rod above and below the valve. These served to break up any caked material which formed in the tank. A pipe at the bottom of the container held a nipple through which nitrogen flowed to purge the system while the tank was being attached to the reactor.

The horizontal copper-tube-bundle condenser on this reactor provided for complete vapor condensation. It was connected to the reactor by a $2\frac{1}{2}$ -inch line and was vented to the atmosphere through a check valve. Condensed vapors were recycled through a liquid check valve to the reactor when the take-off valve in the condensate line was closed. A 2-pound-per-square-inch-pressure relief valve on a T between the reactor and the condenser handled possible surges in the reaction. This valve discharged through the roof to a storage tank which was purged by the stream of nitrogen passing through the system.

The residues from the reaction were carefully alcoholized and pumped into a container from which they were poured into a sand box and quenched with a large volume of water.

The dry box illustrated in figure 4 was used to protect the lithium aluminum hydride from atmospheric moisture and oxygen during handling and grinding. It was equipped with six pairs of rubber gloves sealed to

openings in the sides of the box. The atmosphere within the box was kept sufficiently dry and air free by flushing continuously with a stream of oil-pumped nitrogen which entered through a perforated header encircling the dry box about 3/4 inch from the bottom.

The lithium aluminum hydride was crushed to pebble size in a mortar, then powdered by means of a food blender. The housing for the motor in the base of the blender was enclosed in a metal casing and pressurized with nitrogen in order to minimize the possibility of a spark acting as a source of ignition. This motor and the dry box itself were individually grounded to the aluminum floor on which the equipment rested.

The column used to fractionally distill the combined crude products at atmospheric pressure had a pot capacity of 200 gallons. It was composed of a stainless-steel tube 4 inches in diameter and 100 feet tall packed with 3/8-inch Raschig rings. The construction of this column was similar to that described for the 30-foot column in reference 4.

MATERIALS

Lithium aluminum hydride. - Lithium aluminum hydride, LiAlH_4 , commercially obtained, was furnished as small cakes, which were broken and then pulverized to a fine powder before use. This operation caused the evolution of ether absorbed on the salt.

Dioxane. - The dioxane was purchased in 55-gallon drums and purified by percolation through a 10-foot column of activated alumina. The purified dioxane gave no reaction with lithium aluminum hydride, thus indicating the absence of water, aldehydes, and peroxides.

Butyltrichlorosilane. - The butyltrichlorosilane was purchased from a commercial source and was reported to be a mixture of 50 percent normal butyltrichlorosilane and 50 percent of mixed iso- and secondary butyltrichlorosilanes. When 117 pounds from a drum of discolored reactant was distilled under nitrogen in a 30-foot column rated at about 100 theoretical plates, 21.4 pounds (18.3 percent) boiled at 280.4° to 288.5° F, and 20.4 pounds (17.4 percent) boiled at 288.5° to 296.6° F. A third fraction of 69.8 pounds (59.6 percent) boiling at 296.6° F was shown to be the *n*-butyl isomer by independent synthesis from silicon tetrachloride and *n*-butylmagnesiumchloride. A head fraction of about 2 pounds and a residue of about 3 pounds of material were discarded. A second drum contained water-white material and was used directly without distillation.

Nitrogen. - Oil-pumped nitrogen was used directly from tanks without further treatment.

PROCEDURE

The general procedure used in all the runs in the 50-gallon reactor is illustrated by the following typical preparation: The reactor was cleaned and rinsed with acetone, and the system was then dried with air. The air was replaced with an inert atmosphere of nitrogen by purging the system overnight.

The addition tank and 12.35 pounds (0.326 lb-moles) of lithium aluminum hydride were sealed into the dry box together with the equipment necessary for pulverizing the hydride and sealing off the addition tank. The dry box was purged of air and flushed continuously with nitrogen while the lithium aluminum hydride which had been crushed to pebble size was ground to a fine powder in a food blender. The finely ground lithium aluminum hydride was then sealed into the dry-powder-addition tank. This piece of apparatus could then be safely removed from the dry box.

Meanwhile, 30 gallons of dioxane was pumped into the reactor and stirring was begun. The addition tank was attached to the reactor while a stream of nitrogen flushed the opening. The valve of the addition tank was lifted and turned slowly until all the lithium aluminum hydride had been added to the dioxane. The tank was then quickly removed and replaced with a sealing flange. The temperature of the dioxane slurry was raised to 131° F prior to adding the butyltrichlorosilane in a slow stream over a period of 2 hours until 64.90 pounds (0.34 lb-moles) had been added. The mixture was refluxed for an additional $1\frac{1}{2}$ hours before take-off was begun.

The product was stripped from the reaction mixture slowly at first. Most of the butylsilanes came over in the first 3 gallons of stripped material. A total of 255 pounds of crude material was collected for fractional distillation. After the crude product was stripped from the reactor, 9 gallons of methanol was carefully added to the reactor with stirring. The alcoholized residue was allowed to remain in the reactor several hours before the fluid slurry was drawn off and deactivated in a sand box.

The combined quantity of distillate collected from all the runs amounted to 413 pounds. This was charged into a 100-foot distilling column.

At the beginning of the distillation, a large volume of gas was observed issuing from the vent; therefore, two dry-ice traps were attached to this opening. The material collected in these traps was distilled separately in a small column of about 100 theoretical plates. The head fraction of this forerun was hydrogen sulfide H₂S, which was identified by the lead acetate and cadmium chloride tests. The source of the H₂S

is believed to be the sulfur coating on some of the rubber stoppers used to close the flasks in which lithium aluminum hydride - dioxane slurry was prepared for the small reactor. A second source could have been the distillation column itself. All copper lines were found to have been reduced to a brilliantly pure copper color at the end of the distillation.

Another fraction (14° to 42.8° F) was believed to consist of butane and isobutane. Unfortunately, this material was lost by evaporation before it could be weighed or analyzed. The rest of the material collected in the traps was n-butylsilane and isobutylsilane, which had been entrained in the gases and nitrogen purging stream. The remainder of the material distilled in a normal fashion.

RESULTS

The total over-all yield of final purified product amounted to 80.5 pounds. This was equivalent to a total over-all yield of 82 percent based on the butyltrichlorosilane and does not include handling and distillation losses. The yields obtained as shown by separate purification of products synthesized in the smaller reactor can run as high as 91 percent of butylsilane.

The materials obtained in the fractional distillation of the products are summarized in the following table:

Fraction	Boiling point, °F	Amount, lb	Remarks
I	111.2-116.6	3.5	Heads
II	116.6-118.4	29.5	Low-boiling branched isomers
III	118.4-131.0	4.5	Intermediate
IV	131.0-132.8	38.0	High-boiling <u>n</u> -butyl isomer
V	-----	3.0	Vent trappings
VI	132.8-140.0	2.0	Tails

The ratio of normal to mixed iso- and secondary butylsilanes in the product is about 4:3. The structure of the normal isomer was confirmed by an independent synthesis from pure materials.

CONCLUDING REMARKS

Butylsilanes may be synthesized from butyltrichlorosilanes and lithium aluminum hydride with yields greater than 80 percent in pilot-

plant size equipment. This may safely be accomplished by conducting all operations under an atmosphere of oil-pumped nitrogen and in double-valved sealed containers.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, May 14, 1953

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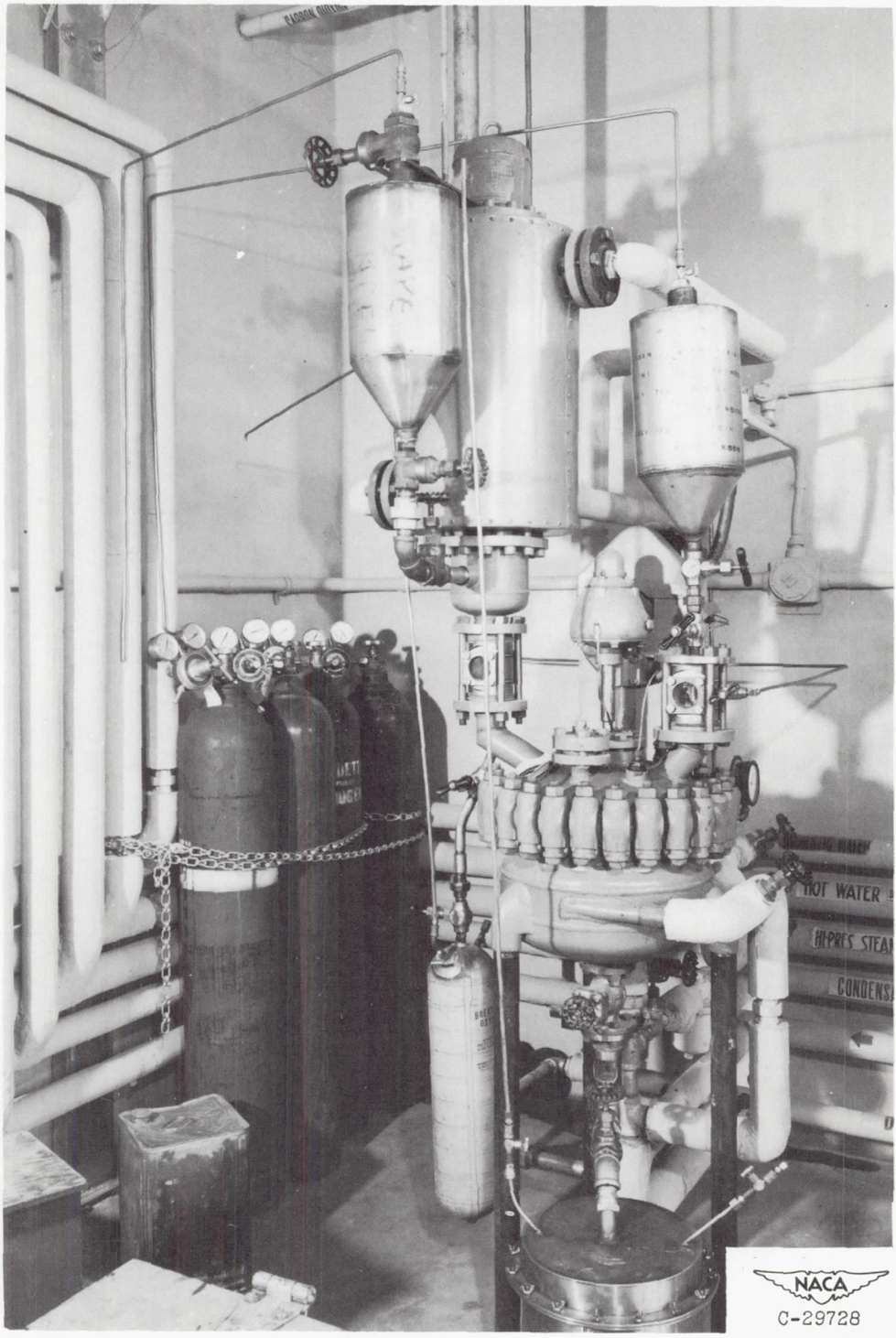
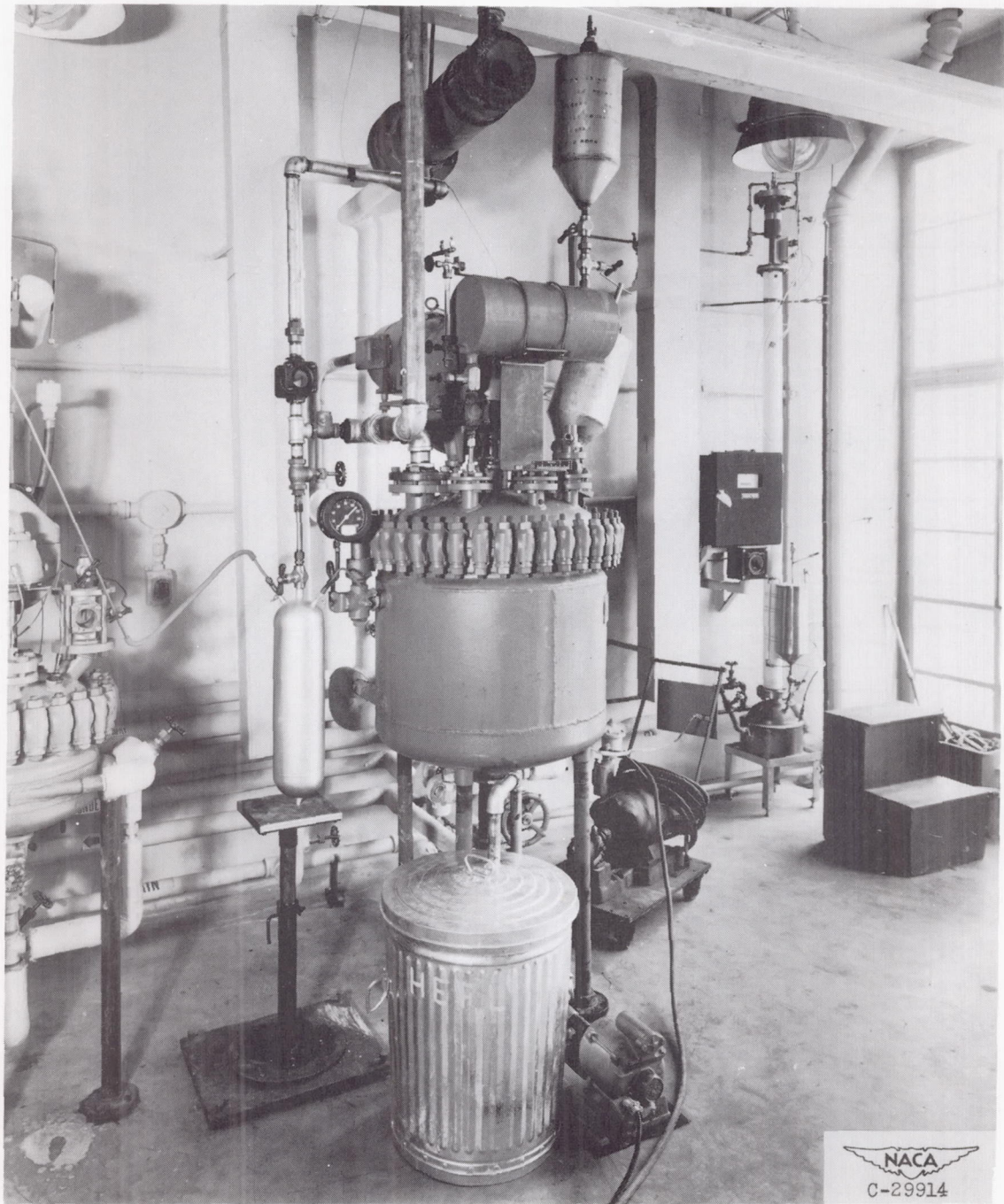


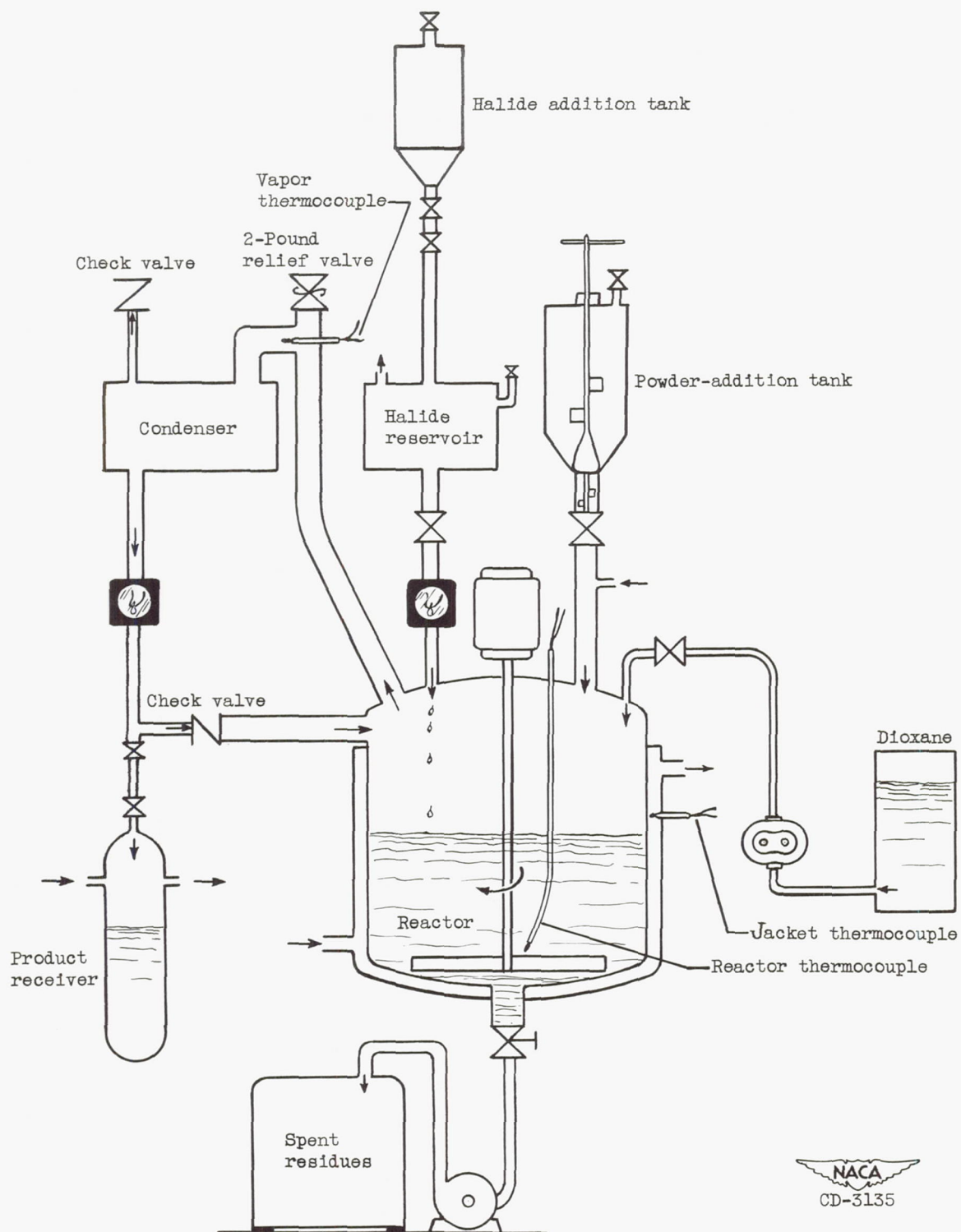
Figure 1. - Five-gallon reactor.



(a) Operational setup.

Figure 2. - Fifty-gallon reactor.

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(b) Schematic diagram.

Figure 2. - Concluded. Fifty-gallon reactor.

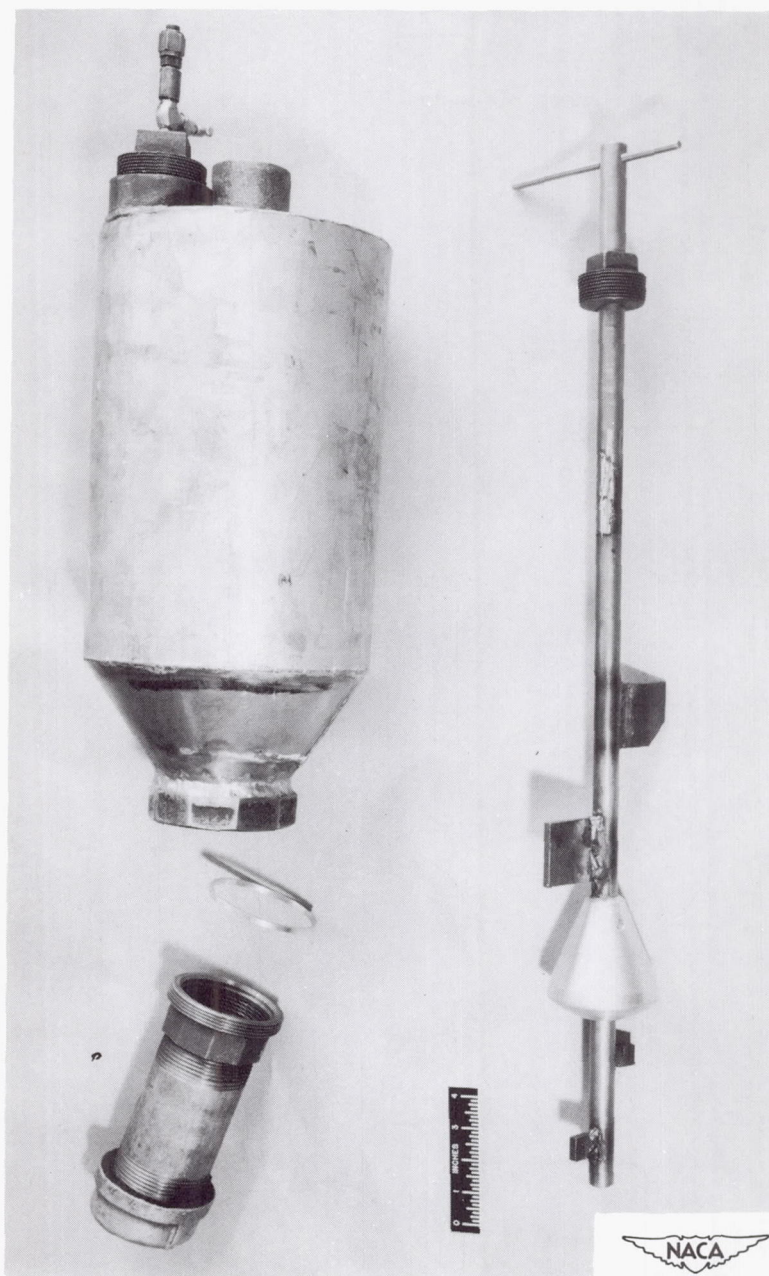


Figure 3. - Powder-addition tank for lithium aluminum hydride.

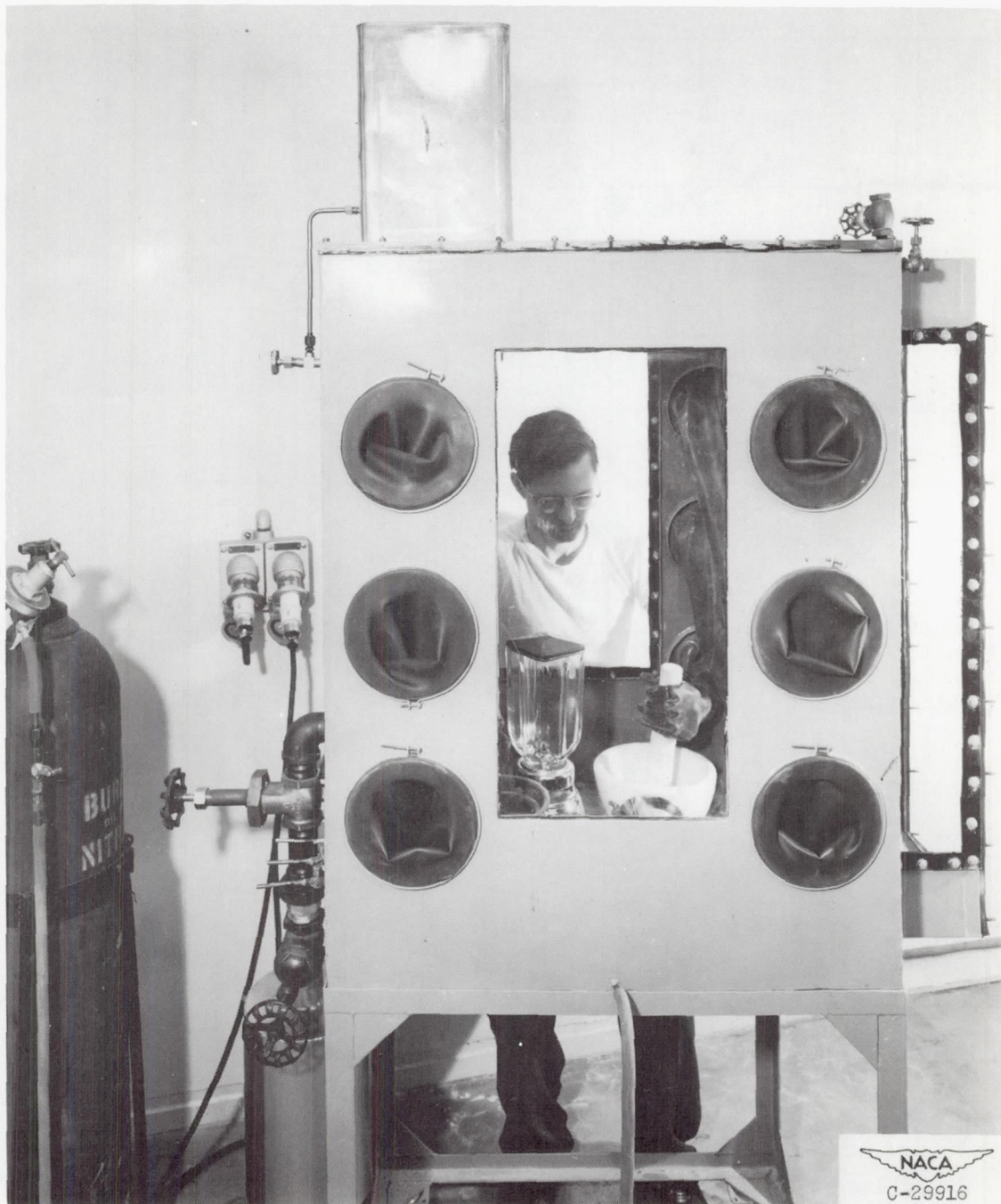
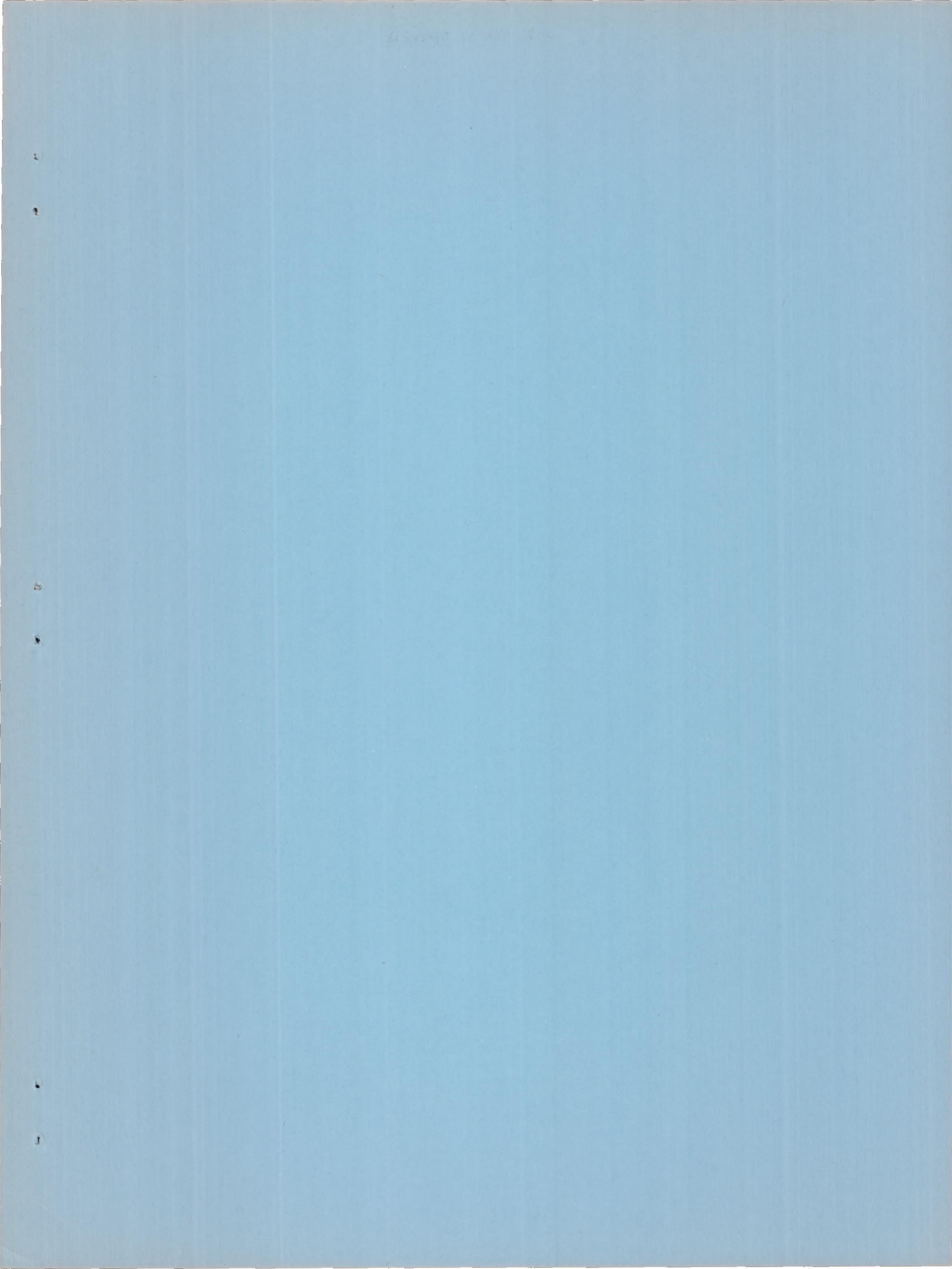


Figure 4. - Dry box.



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