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U. S. NAVAL TECHNICAL MISSION TO JAPAN
CARE OF FLEET POST OFFICE
SAN FRANCISCO, CALIFORNIA

29 November 1945

RESTRICTED

From: Chief, Naval Technical Mission to Japan.
To : Chief of Naval Operations.

Subject: Target Report - Use and Manufacture of Ortho Tolyl Urethane for Stabilizing Rockets and Propellants.

Reference: (a)"Intelligence Targets Japan" (DNI) of 4 Sept. 1945.

1. Article 1 of the report outlined by Target 0-10 of Fascicle 0-1 of reference (a), is submitted herewith.

2. The investigation of the target and target report were accomplished by Lt. Comdr. R.A. Cooley, USNR, assisted by Lt. (jg) F.T. Purdy, USNR, and Lt.(jg) S.H. Kadish, USNR, as interpreters and translators.

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Captain, USN

JAPANESE PROPELLANTS-ARTICLE 1
USE AND MANUFACTURE OF ORTHO TOLYL URETHANE FOR STABILIZING ROCKET AND GUN PROPELLANTS

"INTELLIGENCE TARGETS JAPAN" (DNI) OF 4 SEPT. 1945

FASCICLE O-1, TARGET O-10

NOVEMBER 1945

U.S. NAVAL TECHNICAL MISSION TO JAPAN

SUMMARY

ORDNANCE TARGETS

JAPANESE PROPELLANTS, ARTICLE 1 - THE USE AND MANUFACTURE OF ORTHO TOLYL URETHANE FOR STABILIZING ROCKET AND GUN PROPELLANTS

The reasons why the Japanese Navy adopted a new propellant powder stabilizer originated by Japanese chemists are discussed and the method of large scale manufacture is presented.

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The Report

REFERENCES

Japanese Personnel Interviewed:

Rear Admiral Michizo SENDO, IJN, Professor of Explosives and Propellants, Tokyo Imperial University; and Director of Research, Hiratsuka Naval Powder Factory.

Commander T. MURATA, IJN, Chief Engineer, Hiratsuka Naval Powder Factory.

Technician S. MIYAIRI, Research Chemist, Hiratsuka Naval Powder Factory.

Mr. Aioji AOYAMA, General Director, Hodogaya Chemical Manufacturing Company.

Mr. Einosuke TSUBOUCHI, Manager of General Department, Hodogaya Chemical Manufacturing Company.

Mr. J. HAMAGUCHI, Chemical Engineer, Hodogaya Chemical Manufacturing Company.

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INTRODUCTION

By chromatographic analysis of captured Japanese rocket propellants a stabilizing compound previously not known to be used by any country was found in 1944. This stabilizer was identified as ortho tolyl urethane and stimulated several questions. These were:

1. Was this new stabilizer more effective than those used by other countries?
2. Why had the Japanese chosen the ortho isomer rather than the more easily manufactured para isomer?
3. What manufacturing procedure was used by the Japanese?

Information obtained from the Japanese, pertinent to these questions, is presented in this report.

THE REPORT

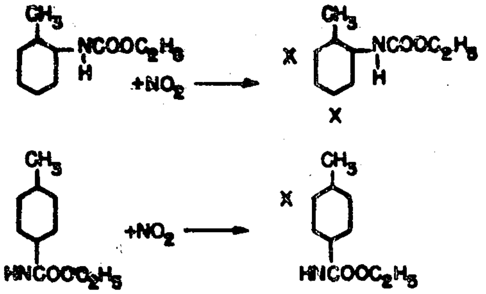
1. Use of Ortho Tolyl Urethane as a Stabilizer

Stability tests had convinced the Japanese Navy that ortho tolyl urethane had a stabilizing power better than Centralite (symmetrical diethyl-diphenylurea--melting point 71°C). Little difference was found in the gelatinizing power of the two. However, because of its lower melting point (42°C), ortho tolyl urethane yielded a powder much easier to manufacture, particularly during rolling and extrusion, than did Centralite.

The Japanese stated that ortho tolyl urethane stabilized powder was so easy to roll and extrude that they had practically none of the danger from fire which has been so troublesome in the American manufacture of rocket propellant.

2. Why the Ortho Isomer Was Used Rather than the Para Isomer

Assuming that the process of decomposition of powder is a matter of the liberation of NO_2, then in accordance with the following reactions:



the ortho isomer can undergo nitration in two positions while the para isomer has only one position in which it is readily nitrated. This was stated to be the principal reason for selecting the ortho rather than the para isomer.

3. The Manufacture of Ortho Tolyl Urethane

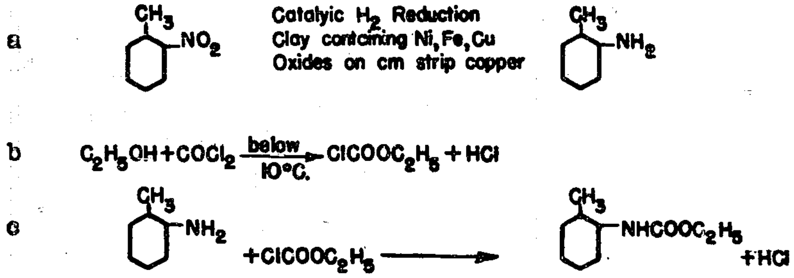
Naval Technician Seitaro MIYAIRI suggested the use of ortho tolyl urethane as a stabilizer about 1927, but it did not come into practical use until about 1933 when Vice Admiral S. HATANO "rediscovered" and became interested in the unusual properties of this stabilizer.

The Hodogaya Chemical Manufacturing Company, experienced in the synthesis of organics and dye stuffs, was asked to undertake the manufacture of ortho tolyl urethane, and apparently their YOKOHAMA plant was the only source of it in the whole of JAPAN. The approximate production figures given for this plant are:

Year	1938	1939	1940	1941	1942	1943	1944	1945
Tons per month (Approx.)	2	2	2	3	4	4	5	5

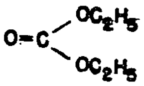
The price charged the Navy was said to be four yen per kilogram in 1938. By 1945 the price had risen to 15 yen per kilogram, at which time Centralite was being sold at about 18 yen per kilogram.

The steps involved in the preparation of ortho tolyl urethane by the Hodogaya Chemical Manufacturing Company are:



Pure ortho nitro toluene for reaction (a) was obtained by vacuum distillation of ortho and para nitro toluene.

Reaction (b) was said to be the most difficult to carry out in practice, and if the temperature was not carefully controlled rather than the ethyl ester of chlorocarbonic acid results.



4. Process of Manufacturing $ClCOOC_2H_5$

Charge:

Ethyl alcohol	320kgs
Phosgene	350kgs
Time for reaction	20 hrs
Temperature	8°C.

Three hundred twenty kilograms of 99 percent ethyl alcohol is introduced into a three liter reaction kettle (See Figures 2 and 3) with a cooling jacket, to be cooled down to 5°C. by circulating brine or cooled water at 1-2°C. Phosgene gas is then carefully blown into it, and during the reaction the temperature of the contents should be kept below 8°C. by continuous cooling and stirring. The absorption of about 350 kilograms of phosgene gas requires about 20 hours. When the reaction is completed, the contents are transferred to washing tanks with stirrers. There it is repeatedly washed with water in order to separate the hydrochloric acid.* A small amount of soda ash is thrown into the oily solution to eliminate the last traces of hydrochloric acid that might remain in the product. After vigorous stirring it is allowed to settle for about two hours. The whole product is then carefully filtered through a good filter paper. The filtrate is the purified product. The yield is about 300 kilograms.

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*From the separated wash water (a dilute alcohol solution) alcohol is recovered by fractional distillation. The theoretical yield of this process is about 80 percent.

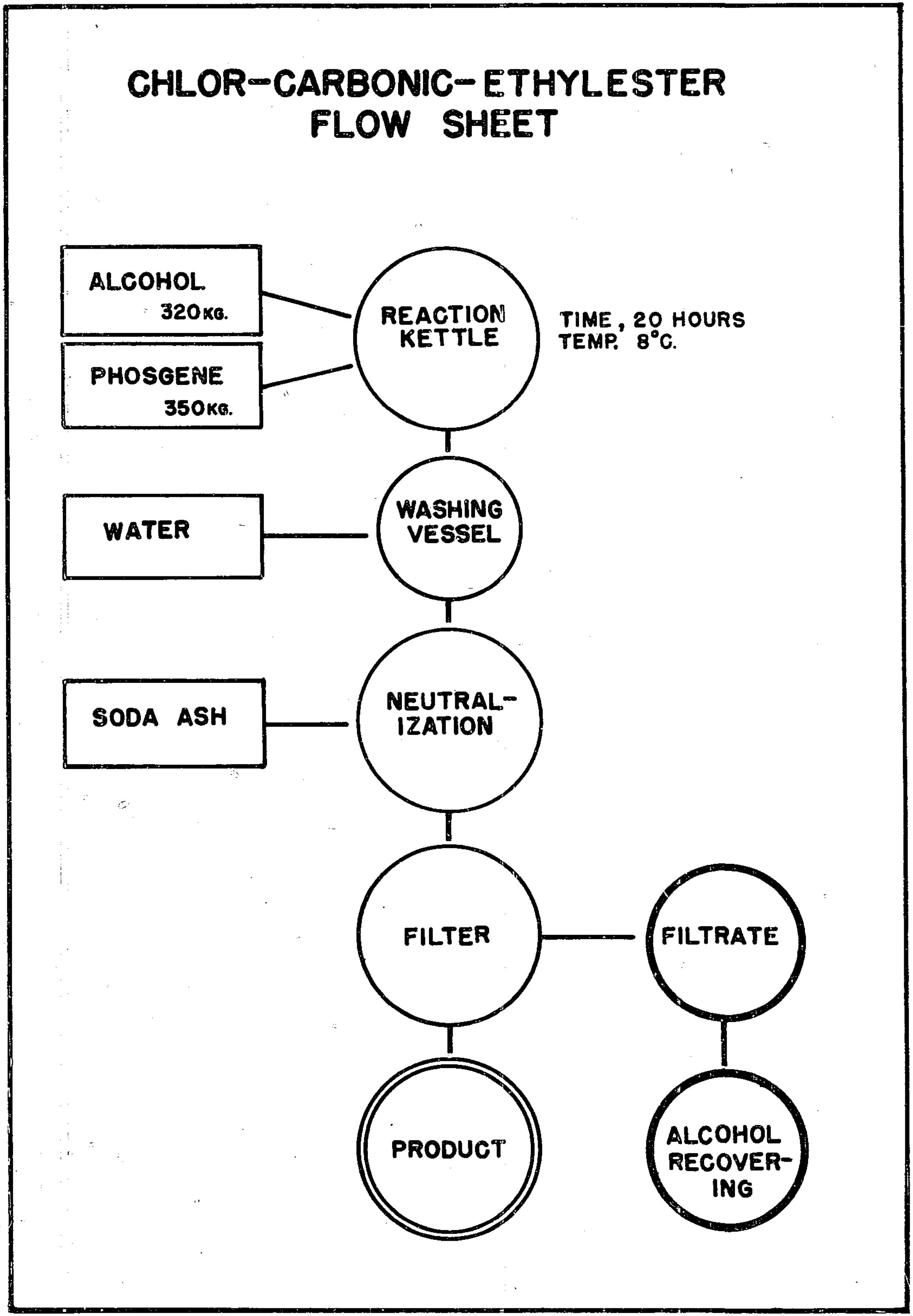
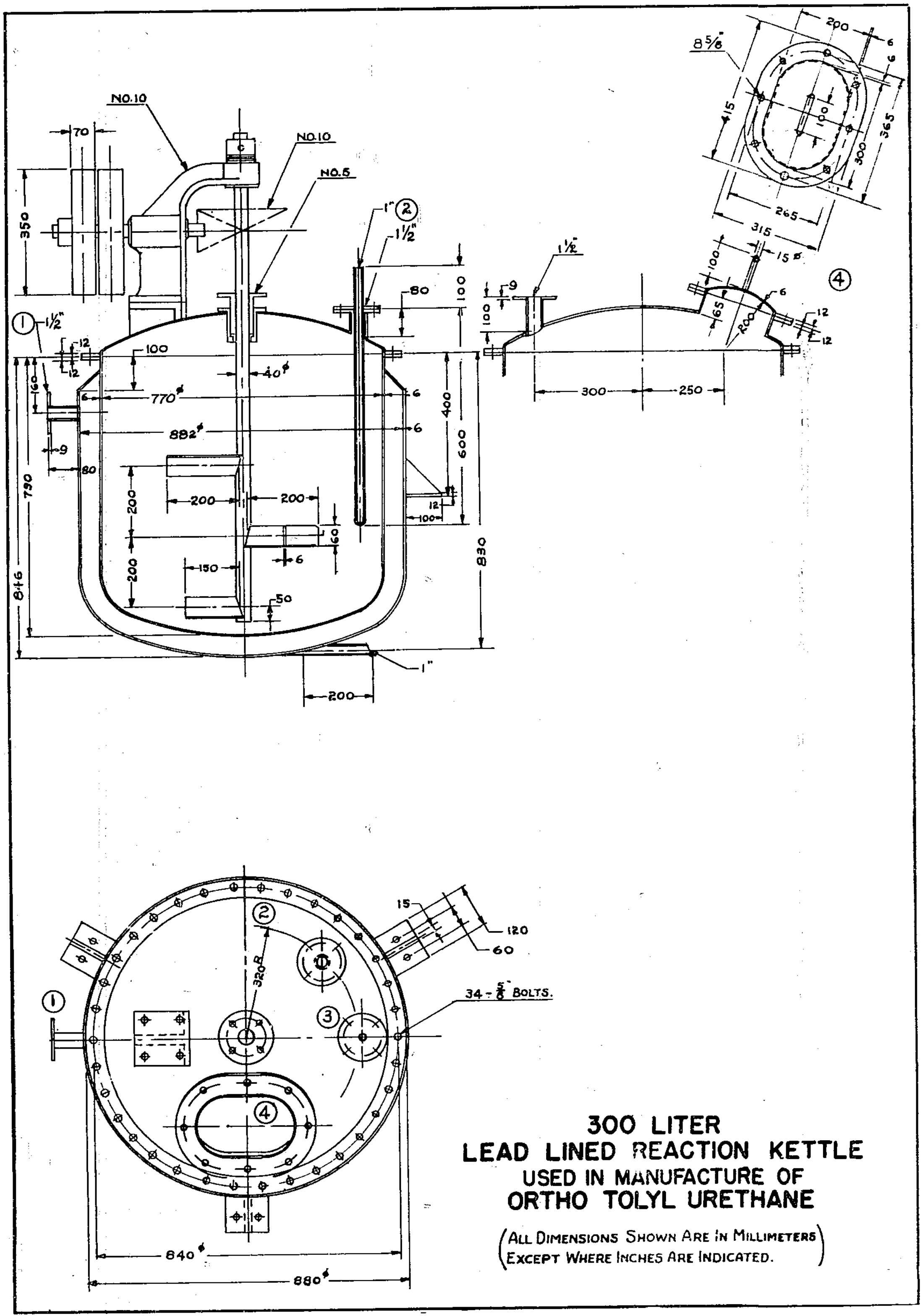

CHLOR-CARBONIC-ETHYLESTER
FLOW SHEET
ALCOHOL 320 KG.
PHOSGENE 350 KG.
REACTION KETTLE
TIME, 20 HOURS
TEMP. 8°C.
WATER
WASHING VESSEL
SODA ASH
NEUTRAL-IZATION
FILTER
FILTRATE
PRODUCT
ALCOHOL RECOVER-ING

Figure 1



300 LITER
LEAD LINED REACTION KETTLE
USED IN MANUFACTURE OF
ORTHO TOLYL URETHANE

(ALL DIMENSIONS SHOWN ARE IN MILLIMETERS
EXCEPT WHERE INCHES ARE INDICATED.)

Figure 2

5. Process for Manufacturing Ortho Tolyl Urethane

Charge:

O-Toluidine	90kgs
Caustic soda so. (45%)	90kgs
Chlorocarbonic acid Ethylester	97.5kgs

Ninety kilograms of O-toluidine and 90 kilograms of caustic soda solution (45 percent) are introduced into the double-jacketed reaction kettle of 500-liter capacity (See Figure 4). Then 97.5 kilograms of chlorocarbonic acid ethylester are slowly and carefully added in a fine stream under continuous stirring and cooling with water. During the reaction the inner temperature should be maintained at 35-40°C.

The pouring of chlorocarbonic acid ethylester is to be ended in seven to eight hours, after which stirring must be continued one more hour in order to complete the reaction. The contents are then heated to 80°C. and poured into 300 liter iron tanks, each of which contains about 100 liters of cold water. A greyish white product crystallizes out.

This crude product is washed with a dilute H_2SO_4 water solution (Ca three percent) three or four times in the melted state to catch the remaining o-toluidine, and is crystallized by cooling. The washed crystals are then dissolved in 12 to 16 kilograms of alcohol, and cooled. Ortho tolyl urethane then separates out in clean, white crystals, which are crushed and separated with a centrifuge. The yield is 105 kilograms.

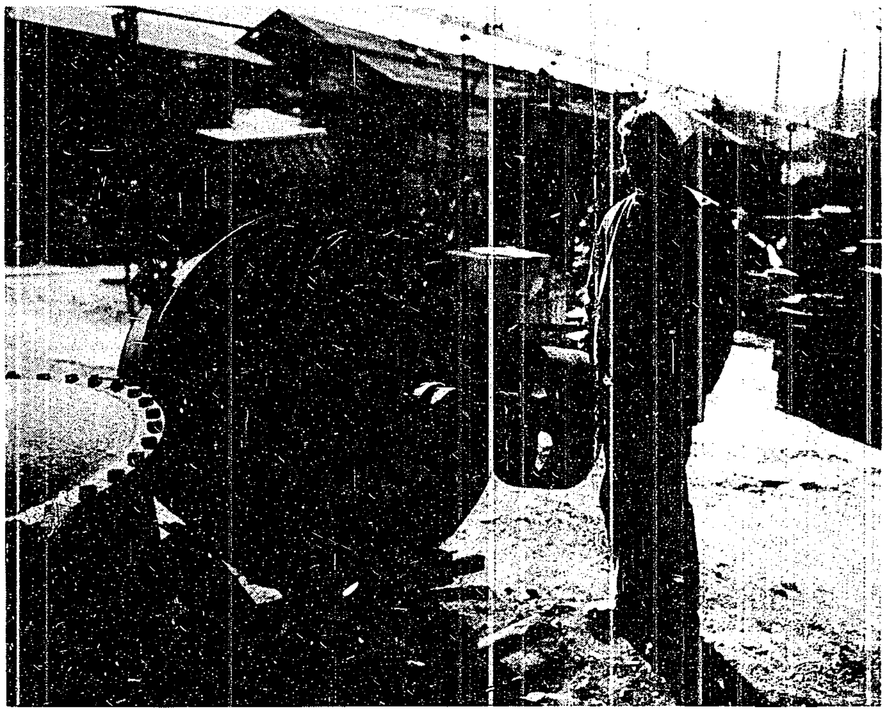


Figure 3

Typical 300 Liter Lead-Lined Reaction
Kettle Used in Manufacture of
Ortho Tolyl Urethane

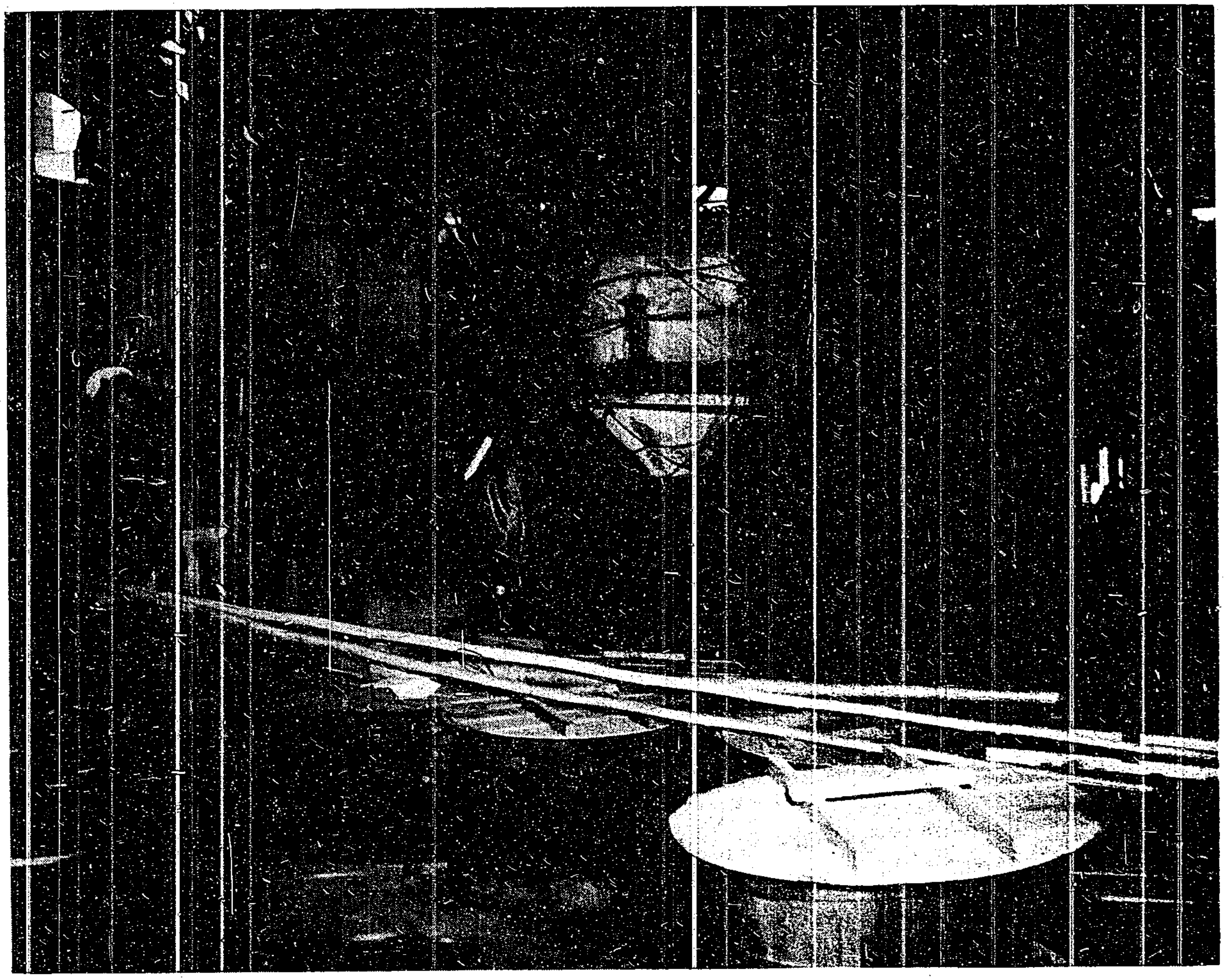


Figure 4

View of Chlorocarbonic Acid Ethylester and
Ortho Toluidine Reaction Kettle (background)
With Crystallizing Tubs (foreground)

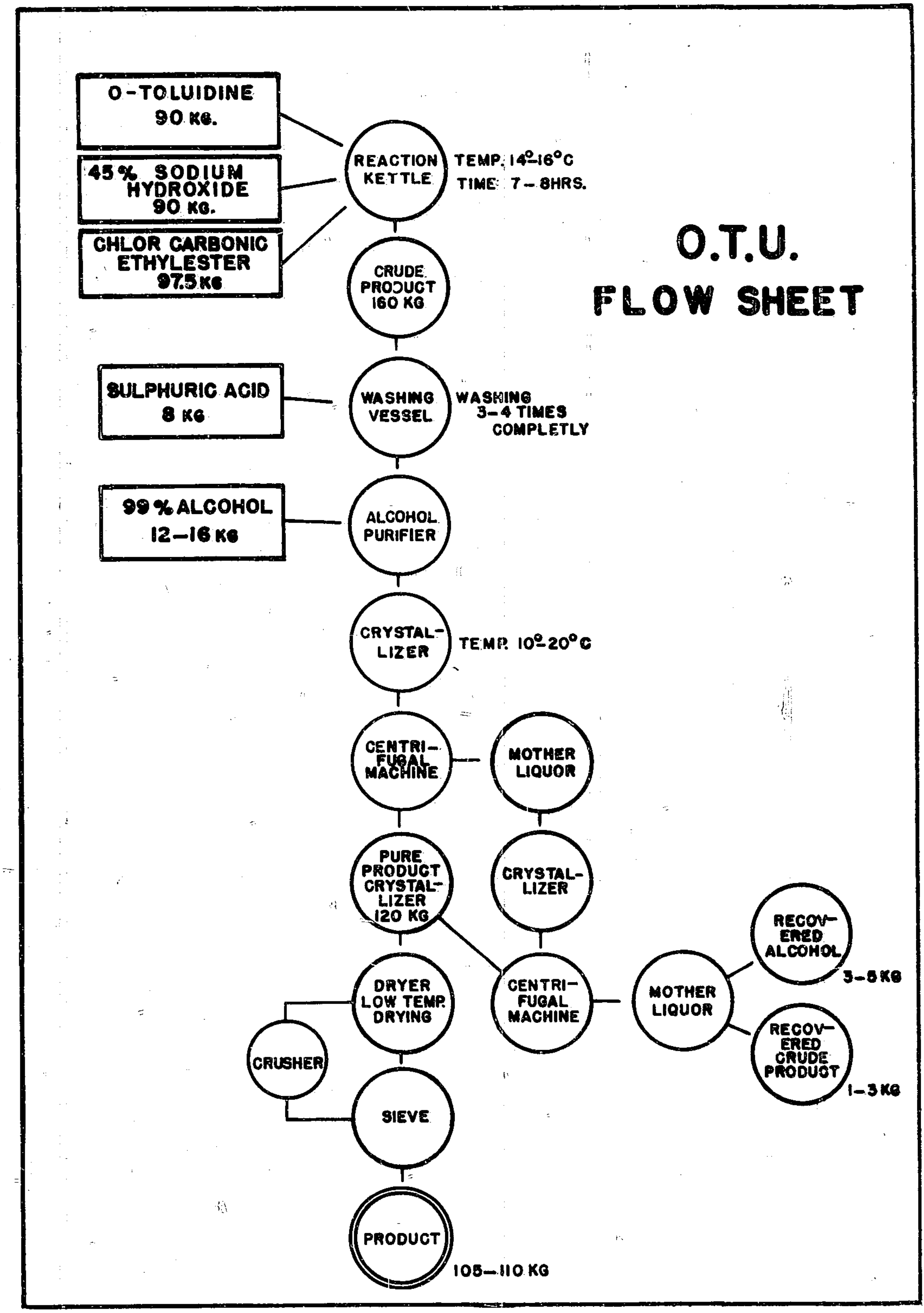

O.T.U.
FLOW SHEET
O-TOLUIDINE 90 KG.
45% SODIUM HYDROXIDE 90 KG.
CHLOR CARBONIC ETHYLESTER 97.5 KG
REACTION KETTLE
TEMP. 14°-16°C
TIME 7-8HRS.
CRUDE PRODUCT 160 KG
SULPHURIC ACID 8 KG
WASHING VESSEL
WASHING 3-4 TIMES COMPLETLY
99% ALCOHOL 12-16 KG
ALCOHOL PURIFIER
CRYSTAL-LIZER
TEMP. 10°-20°C
CENTRI-FUGAL MACHINE
MOTHER LIQUOR
PURE PRODUCT CRYSTAL-LIZER 120 KG
CRYSTAL-LIZER
DRYER LOW TEMP. DRYING
CENTRI-FUGAL MACHINE
MOTHER LIQUOR
RECOV-ERED ALCOHOL
3-5 KG
RECOV-ERED CRUDE PRODUCT
1-3 KG
CRUSHER
SIEVE
PRODUCT
105-110 KG

Figure 5

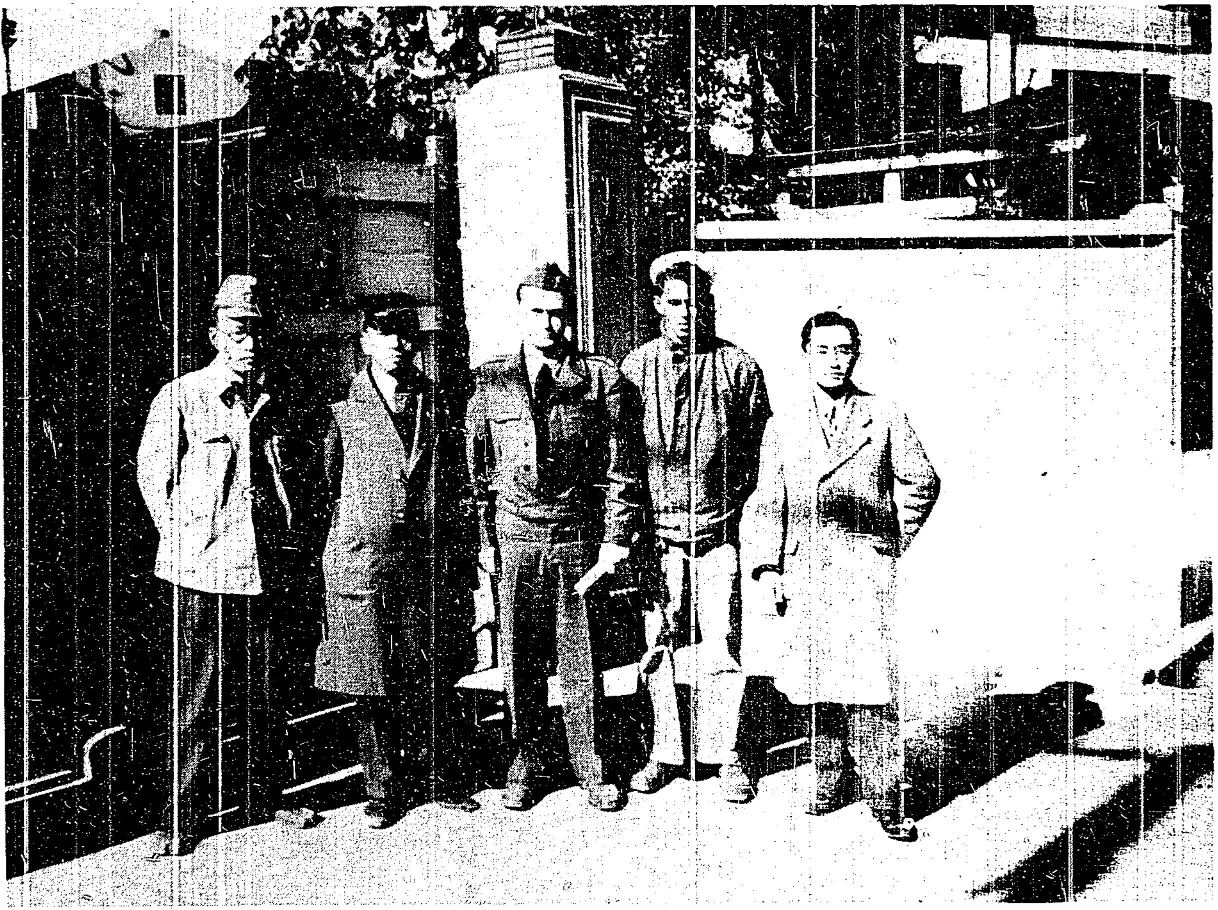


Figure 6

Hodogaya Chemical Engineers and NavTechJap Inspection Party at Hodogaya's YOKOHAMA Factory

Left to right: J. Hamaguchi, Chemical Engineer, Aioiji AOYAMA. General Director, Hodogaya Co., Lt. Comdr. R. A. Cooley USNR, Eckert Sm2c USN, Einosuke TSUBOUCHI, Manager of the General Department.