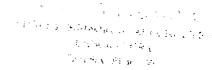# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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THE PREPARATION OF 2,2,4,4-TETRAMETHYLPENTANE

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# NACA

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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RESTRICTED BULLETIN

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THE PREPARATION OF 2,2,4,4-TETRAMETHYLPENTANE

By N. L. Drake

The reactions involved can be formulated briefly as follows:

I. $\left.\begin{array}{l} (CH_3)_3CCH_2C\diagup_{CH_3}^{CH_2} \\[2ex] (CH_3)_3C-CH = C(CH_3)_2 \end{array}\right\} + HCl \xrightarrow{-20^\circ} (CH_3)_3CCH_2CCl(CH_3)_2$

II. $CH_3I + Zn(Cu) \longrightarrow CH_3ZnI + Cu$

$2CH_3ZnI \xrightarrow{50^\circ - 210^\circ} Zn(CH_3)_2 + ZnI_2$

III. $(CH_3)_3CCH_2CCl(CH_3)_2 + Zn(CH_3)_2 \xrightarrow{C_6H_6} (CH_3)_3CCH_2C(CH_3)_3 + CH_3ZnCl$

IV. $ZnI_2 + (CH_3)_2SO_4 \xrightarrow[CaCO_3]{heat} 2CH_3I + ZnSO_4$

Seven distinct operations are involved:

1. Preparation of di-isobutylene hydrochloride (reaction I above)

2. Preparation of dimethylzinc (reaction II)

3. Reaction of dimethylzinc in dry benzene with di-isobutylene hydrochloride (reaction III)

4. Preliminary distillation of the reaction products

5. Treatment of the first distillate, (4), with sodium and alcohol

6. Final distillation after appropriate washing of
   the products from (5)

7. Recovery of the iodine in the zinc residues of
   II (above) as methyl iodide

Each of these operations is described below.

## THE PREPARATION OF DIMETHYLZINC

### A. Preparation of the Zinc-Copper Couple

The couple is prepared in an automatic machine devised for
this purpose and shown in figure 1. It consists of an electric
furnace made by winding a heating element of 31 feet of nichrome
wire (B. & S. No. 18, resistance 0.992 ohms/ft) around a piece
of galvanized iron pipe covered with three layers of heavy as-
bestos paper. The resistance wire is embedded in alundum cement
and the whole lagged with magnesia-asbestos pipe covering held
in place by a piece of galvanized iron stovepipe. The length of
the heated portion of the furnace is 37 inches. When a current
of 3.3 amperes is passed through the heating element, the tem-
perature in the interior of the rotating tube is approximately
that necessary for the preparation of the zinc-copper couple;
regulation can be accomplished by means of a variable transformer
in the heating circuit.

Axially through the furnace passes a 25-millimeter pyrex
tube, which is rotated during preparation of the couple by a
belt drive to a wooden pulley near the open end of the tube. A
loosely fitting Bunsen clamp and a 29/42 standard taper ground-
glass joint serve as bearings for the rotating tube. The fur-
nace and its appertenances are held at an angle of about $5^{\circ}$ from
horizontal by means of suitably placed supports of which two
Bunsen clamps only are shown in figure 1. The female part of
the joint, which serves as a bearing, is part of a T-tube so
arranged that material flowing by gravity down through the fur-
nace will discharge into a 3-liter round-bottomed flask. The
branch of the T-tube passes through a rubber stopper, which is
wired tightly in the neck of the flask; a 7-millimeter glass
tube also passes through this stopper and provides a means of
passing hydrogen gas into the system.

The charge is forced into the rotating tube by means of a
worm, which operates in an 18-millimeter glass tube to which is
attached a hopper. The zinc-copper oxide mixture is picked up

by the worm at the bottom of the hopper and forced into the rotating tube; the mixture then passes slowly through the rotating tube and discharges eventually into the 3-liter flask. Dry hydrogen enters the furnace through the tube previously mentioned, proceeds counter-current to the charge, and escapes together with the water formed by the reaction through the small annular space between the wall of the rotating tube and the wall of the feed tube. A belt drive to the pulley wheel near the end of the rotating tube turns the tube at about 9 rpm, and a flexible shaft drive turns the worm at about 2 rpm. Glass wool is packed between the rotating tube and the iron furnace pipe to prevent convection currents through the furnace.

A cork hammer pulled sharply against the rotating tube by a spring, and actuated by a motor-driven cam three or four times per minute helps to prevent particles from sticking to the side of the rotating tube during preparation of couple. This device (not shown in fig. 1) operates on that part of the rotating tube adjacent to the ground-glass bearing.

With the rotating tube in place, the furnace is heated for 5 hours (preferably over night) before use. (The temperature within the upper half of the rotating tube as measured by a thermocouple while hydrogen is flowing through the tube is $396^{\circ}$ -$421^{\circ}$.)*

After the initial heating period, the rest of the apparatus is assembled and hydrogen is passed through the furnace for 1 to $1\frac{1}{2}$ hours at a rate of 120 to 130 milliliters per minute. A uniform mixture of 120 grams of powdered cupric oxide and 960 grams of zinc dust is poured into the hopper and the machine started. When properly adjusted, the entire charge can be reduced in 5 to 6 hours and no further attention need be given to the machine. Now and then the reduced mass may stick to the sides of the rotating tube; when this happens it is necessary to loosen the mass by scraping the sides of the tube carefully with a metal scraper (a piece of 3-mm welding rod). When all the charge has passed through the furnace, the receiver is removed, quickly stoppered, and attached to the apparatus used in the preparation of dimethylzinc.

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*All temperatures are in degrees Centigrade.

### B. The Treatment of the Couple with Methyl Iodide

The apparatus employed for bringing about reaction of the couple with methyl iodide is shown in figure 2. This apparatus consists of two parts. The part in which dimethylzinc is prepared is a 3-liter round-bottomed flask closed with a well-rolled cork and provided with a reflux condenser; the flask is supported in an oil bath that can be heated electrically. The other part of the apparatus is a 5-liter, round-bottomed, three-necked flask provided with a mechanical stirrer (sealed), a 500-milliliter dropping funnel, and a reflux condenser. The flask is supported in an insulated tub, which can serve as an ice bath or a hot-water bath. The two parts of the apparatus are so assembled that the tops of the condensers can be joined by a "bridge" of glass tubing provided with outlets as shown. Rubber stoppers can be used in this apparatus only where indicated.

Note: The entire apparatus must be dried thoroughly by baking in an oven before use. When the apparatus is removed from the oven, it is assembled at once and protected from the access of moisture by drying tubes containing drierite.

After the apparatus has been assembled, air is displaced from it by dry carbon dioxide, and the flask containing the zinc-copper couple is attached by means of a carefully chosen, well-rolled cork; the cork is then coated with shellac. The oil bath is heated to 45°-46° and 1100 grams (8 moles) of dry, methanol-free methyl iodide is added through the top of the bridge. Reaction begins after several hours whereupon the reflux rate increases markedly. Refluxing is continued over night (approx. 14 hr). The temperature of the oil bath is then raised to 48° -49° and refluxing is continued for 7 or 8 hours longer. During the entire period, a slow stream of carbon dioxide is passed through the apparatus. Some dimethylzinc is formed during this time, but the bulk of the product is methylzinc iodide.

Caution: Dimethylzinc is spontaneously inflammable in the air and the zinc oxide formed by the combustion is highly toxic. All the operations in which dimethylzinc is used must be carried out under an inert gas such as carbon dioxide or nitrogen.

When the formation of methylzinc iodide is complete, the carbon dioxide inlet used during the reaction is closed. Five hundred milliliters of dry benzene is introduced into the three-necked flask through the separatory funnel and carbon dioxide is

then swept across the opening of the separatory funnel by means
of a T-tube. The temperature of the oil bath is then raised
gradually, the water is emptied from the reflux condenser, and
the dimethylzinc· is distilled into the 5-liter three-necked
flask containing the benzene. The temperature of the oil bath
is raised to 210° at a uniform rate over a period of 2 or 3
hours; more rapid heating should be avoided. The last of the
dimethylzinc is driven into the benzene by passing steam through
the empty condenser.

## THE PREPARATION OF 2,2,4,4-TETRAMETHYLPENTANE

When the distillation of the dimethylzinc is finished, the
oil bath is allowed to cool undisturbed for at least 1/2 hour..
The stopcock of the dropping funnel, which was open during the
distillation, is then closed and the carbon dioxide inlet tube
again attached at the top of the bridge where it was during the
preparation of methylzinc iodide. The rate of carbon dioxide
flow is increased considerably and the stopper pulled very
quickly from the opening at the top of the bridge and replaced
by a vent tube leading outside the building. A rather rapid
stream of carbon dioxide is necessary to prevent combustion of
dimethylzinc fumes remaining in the apparatus; it is to de-
crease the amount of dimethylzinc in the apparatus near the
opening that the oil bath is allowed to cool for 1/2 hour be-
fore removing the stopper at the top of the bridge.

Di-isobutylene hydrochloride (744 grams) dissolved in dry
benzene (750 ml) is then added through the dropping funnel to
the flask containing the dimethylzinc-benzene mixture at such
a rate that the entire quantity is added over a period of about
4 hours. Too rapid addition of the chloride causes the forma-
tion of a sticky curdy precipitate, which prevents proper stir-
ring; the chloride should therefore not be added too rapidly.
During the addition of the chloride, the flask containing the
dimethylzinc is cooled in a bath of ice and water.

When all the chloride has been added, the mixture is
allowed to stand over night whereupon the water bath around
the three-necked flask is heated by means of live steam to 95°.
After the mixture has been heated with stirring for about 1
hour, 200 milliliters of water is added very slowly through the
separatory funnel. The rate of addition of the water should not
be so rapid that loss of benzene occurs through the reflux con-
denser; the water should, however, be added at the end of the

reflux period without waiting for the water bath to cool. After the water has been added, a mixture of 300 milliliters of concentrated hydrochloric acid and 200 milliliters of water is added. Stirring should be continued until the contents of the flask are thoroughly mixed and the majority of the zinc chloride has dissolved.

Any dimethylzinc or methylzinc iodide remaining in the flask from which the dimethylzinc was distilled is next destroyed by adding water cautiously through the top of the bridge. When this has been done, the carbon dioxide stream can be shut off and the reaction flasks removed. The zinc iodide residues are later worked up for their iodine content. (See preparation of methyl iodide.)

When the reaction product has cooled, the aqueous layer is separated from the benzene layer and the latter is washed with two 200-milliliter portions of water. The benzene is then removed by distillation through a short fractionating column. (A column 20 mm in diameter and 2 ft long packed with glass helices is satisfactory.) The fraction up to 90° is collected, purified as described below under Purification of Recovered Benzene and used again. The fraction from 90° to 125° is collected separately and purified further as described below. This fraction contains a small quantity of benzene, some di-isobutylene, 2, 2, 4, 4-tetramethylpentane and a small amount of di-isobutylene polymer.

The product from three such runs is placed in a 5-liter round-bottomed flask provided with a reflux condenser and mixed with 1 liter of absolute alcohol. One hundred grams of clean sodium is then added in small pieces through the condenser. The rate of addition of the sodium should be such that the mixture refluxes gently. When all the sodium has been added, the flask is heated under reflux for 12 hours; an oil bath is used for heating. The flask with condenser attached is removed from the oil bath and 1 liter of water is added very slowly through the condenser. The addition of the water generates considerable heat and should be carried out cautiously. The addition of water causes the contents of the flask to separate into two layers. The aqueous layer is removed and discarded; the hydrocarbon layer is washed with three 1-liter portions of water and dried by distilling off the hydrocarbon-water azeotrope using the usual type of trap to return the hydrocarbon to the distilling liquid.

The dry hydrocarbon mixture is fractionally distilled. Any efficient column might be used; in the present work, a column

150 by 4.1 centimeters packed with glass helices (3 and 4 turn) was employed. The forerun (up to 120°) is taken off at a 30:1 reflux ratio, the product at a 10:1 reflux ratio. The product is collected in two fractions, from 120° to 122° and from 122° to 122.5°. The fraction, which boils at 122°-122.5°, contains about 98.6 percent of 2,2,4,4-tetramethylpentane (determined by assuming that the freezing point of the hydrocarbon, -66.60°, is lowered 0.37° by each percent of impurity).

The average yield from the three combined runs is 1920 milliliters (640 ml/run), 45 percent of the amount theoretically possible based on the methyl iodide used. The average purity of the entire lot is 97 percent; the fraction boiling at 122°-122.5° represents about 90 percent of the total yield.

### C. The Preparation of Methyl Iodide from the

### Zinc Iodide in the Zinc Residues

The residue from the preparation of dimethylzinc is transferred to a 12-liter round-bottomed flask and water is added to make a total volume of 5 liters. By adding a liter of water to the zinc cake in the original reaction flask and warming the mixture on the steam bath for several hours, the hard cake is sufficiently loosened so that it can be transferred to the 12-liter flask by means of a metal funnel and a poker.

Three hundred and thirty-three grams of potassium iodide and 25 to 50 grams of calcium carbonate are introduced into the flask containing the zinc residues. The flask is supported in a water bath and provided with a stopper, a Hirshberg stirrer, a 500-milliliter dropping funnel, and a connection to a suitable condenser. The condenser must have a large capacity and be supplied with ice water or very cold water. In this work a condenser made from a straight piece of 3/4-inch copper pipe 58 inches long was employed. A coil condenser or a multiple-tube condenser would serve better. The outlet of the condenser is supplied with an adjustable adapter that reaches nearly to the bottom of the receiver and a 3-liter round-bottomed flask that contains a small amount of ice water and is supported in a bath of ice water.

The water bath is brought to boiling and the stirrer is started. After the stirrer has been running for about 5 minutes, addition of dimethyl sulfate through the dropping funnel

is begun. Twelve hundred milliliters of dimethyl sulfate is added over a period of about 15 minutes. During the distillation of the methyl iodide, the adapter at the end of the condenser should be so adjusted that it does not dip into the methyl iodide layer but does extend below the surface of the water.

The average yield of crude methyl iodide is 535 milliliters. The crude product is washed twice with 200-milliliter portions of ice water, dried over anhydrous calcium chloride, and distilled in an apparatus exactly like that used in the first separation of benzene and 2,2,4,4-tetramethylpentane. A reflux ratio of 10:1 is employed and the first 10 milliliters of distillate is rejected and combined with the next batch of crude methyl iodide. Methyl iodide forms an azeotrope with methyl alcohol, which boils at $39^{\circ}$ and contains 25.6 mole percent of methyl alcohol; the rejection of the first 10 cubic centimeters of distillate removes traces of alcohol, which may have escaped removal in the water washing. The purified methyl iodide has a boiling range of about $1/2^{\circ}$. (See Organic Syntheses. Vol. XVIII. John Wiley & Sons., Inc., Oct. 1938, p. 88.)

## PREPARATION OF DI-ISOBUTYLENE HYDROCHLORIDE

Dry hydrogen chloride is passed into commercial di-isobutylene in the presence of anhydrous zinc chloride while the reaction mixture is well stirred and maintained at a temperature of about $-20^{\circ}$ by means of a bath of denatured alcohol cooled by the addition of dry ice.

Hydrogen chloride is available in cylinders at present from at least two companies; if gas in cylinders is not available, the procedure described below may be used for the generation of dry hydrogen chloride.

A 12-liter round-bottomed flask is provided with an efficient sealed stirrer, a 5-millimeter glass inlet tube through which sulfuric acid is siphoned from a reservoir, and an outlet for hydrogen chloride leading to a drying chamber filled with calcium chloride. From this chamber the gas is passed in succession through an empty trap, a sulfuric acid washing bottle, another empty trap, and finally through an 8-millimeter glass tube to the bottom of the reaction flask. Provision is made

for conducting exit gases through an empty trap, a sulfuric acid trap, an empty trap, and finally into water. The hydrogen chloride generator is charged with 3 kilograms of sodium chloride and about 5.7 liters of commercial muriatic acid; the sulfuric acid reservoir is filled with 8 liters of concentrated sulfuric acid.

The reaction flask is charged with 9.5 liters of commercial di-isobutylene and 210 grams of anhydrous zinc chloride and the stirrer is started. Dry ice is added to the cooling bath and when the bath has cooled to $-20^{\circ}$ the generation of hydrogen chloride is started by beginning the addition of sulfuric acid to the salt-muriatic acid mixture; the sulfuric acid can be added rather rapidly at first. After about 1 hour, the rate of bubbling in the sulfuric acid trap beyond the reaction flask slows down as the air is expelled from the apparatus and then starts to speed up again. At this point the rate of addition of sulfuric acid should be slowed down until practically no hydrogen chloride is escaping through the sulfuric acid beyond the reaction vessel. As the reaction proceeds, the rate of absorption of hydrogen chloride increases and it is possible to add the sulfuric acid to the muriatic acid-salt mixture in a steady stream; at this point the hydrogen chloride can be added about as it can be generated. It is necessary to watch the temperature of the cooling bath very carefully during the period of rapid absorption for considerable heat is evolved. More dry ice is added as needed.

After about 6 liters of sulfuric acid has been added to the generator, the rate of absorption declines until no more hydrogen chloride is absorbed (about 7 liters of sulfuric acid are used). The generator is then disconnected and <u>dry</u> air is blown through the di-isobutylene hydrochloride as rapidly as possible without causing entrainment of sulfuric acid from the traps. The air stream is continued until no more hydrogen chloride can be removed. About 24 hours are required to blow out the excess hydrogen chloride; during this time the temperature of the bath is maintained at about $0^{\circ}$. It is not possible to pass air through the mixture until <u>no</u> fuming occurs at the outlet from the reaction vessel; the chloride itself will fume in warm moist air.

The product is removed from the reaction vessel and stored over anhydrous sodium carbonate in brown bottles in a refrigerator.
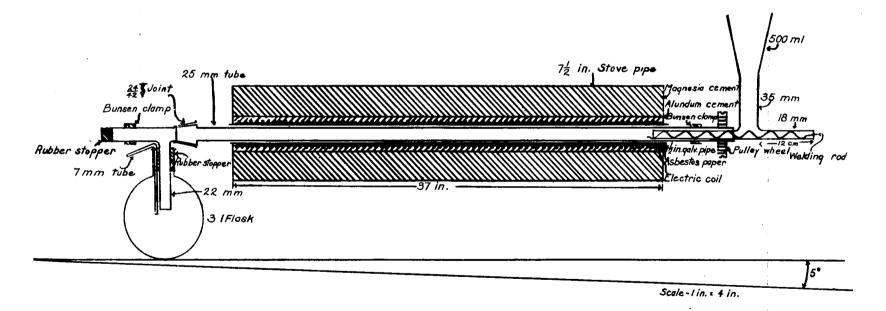
Chloride made in this way can be used without further purification in the preparation of 2,2,4,4-tetramethylpentane.
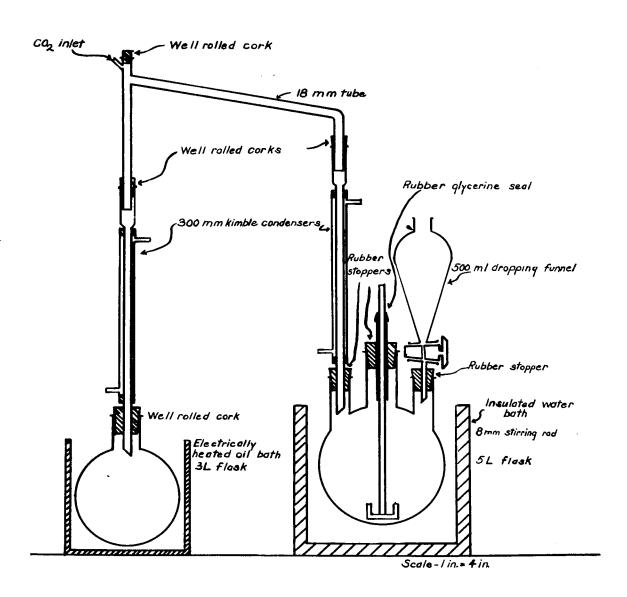
## PURIFICATION OF RECOVERED BENZENE

The benzene used as solvent can be recovered in a condition suitable for use in this process by distilling it from an excess of triethanolamine. The distillate thus obtained is washed carefully with water until it is neutral to litmus and then dried by distilling off the azeotropic water–benzene mixture using the usual form of water trap. The benzene thus dried is stored over sodium ribbon and decanted from the sodium directly into the reaction flask when needed. The benzene contains some di-isobutylene but is satisfactory for use in the reaction above.


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# Fig 1

# COUPLE MACHINE



Labels within the figure:

- 500 ml
- 7½ in. Stove pipe
- Magnesia cement
- 35 mm
- Alundum cement
- 18 mm
- Bunsen clamp
- 12 cm
- 25 mm tube
- 24/42 Joint
- Bunsen clamp
- Rubber stopper
- 7 mm tube
- Rubber stopper
- ½ in. galv. pipe
- Pulley wheel
- Welding rod
- Asbestos paper
- Electric coil
- 22 mm
- 37 in.
- 3 l Flask
- 5°
- Scale - 1 in. = 4 in.

Fig. 1

# Fig 2

# APPARATUS



CO₂ inlet — Well rolled cork

18 mm tube

Well rolled corks

300 mm kimble condensers

Rubber glycerine seal

Rubber stoppers

500 ml dropping funnel

Well rolled cork

Electrically heated oil bath 3L flask

Rubber stopper

Insulated water bath

8mm stirring rod

5L flask

Scale - 1 in. = 4 in.