CO_2	18%
CO	3%
H_2	60.4%
CH_4	0.3%
N_2	20.3%

For 8300 m^3 per hour of gas, the following utilities are required:-

Electricity, high voltage,	150 KW
low voltage,	35 KW
River Water	70 tons
Steam, low pressure	0.5 tons

The catalyst has a life of more than three years.

Three men per shift are required to operate the plant.

The same plant can operate on other gases containing up to 50% hydrocarbons, figured as CH_4. If the feed gas contains more hydrocarbons, part of the synthesis gas is recycled as a diluent.

This process has the advantage that it can be carried out with gases containing sulfur, since the conversion temperature can be raised easily so high that the nickel catalysts are not poisoned.

The formation of carbon is troublesome, but this difficulty can be overcome, probably by changing the design of the combustion chamber.

When gas is manufactured for the methanol synthesis, only oxygen is used and the feed gas must be low in nitrogen.

C. Production of hydrogen Peroxide by Propane Oxidation.

The following brief description of this process was obtained from Dr. Bartholome.

Propane is preheated to a temperature of 350 to 450°C. and admixed with 5 to 10% by volume of oxygen. This mixture flows into an empty reaction chamber where it remains for about 10 seconds, 90% of the oxygen reacting in this interval. The reaction gases are cooled to give an aqueous product containing 30-37% of peroxides. Approximately 50% of these peroxides are organic and the remainder is hydrogen peroxide, which is equivalent to a conversion of about 25% of the oxygen. The dry gas analyzes about 90% propane and 10% propylene.

The reaction vessel consists of apparatus glass "Duran" or of quartz.

These experiments were carried out on a scale of 300 liters of propane per hour.

D. Production of Acetylene by Oxidation of Ethane.

The following information was obtained from Dr. Sachsse. Additional details were not obtained due to the similarity of these experiments to the process of converting methane to acetylene. (See Ludwigshafen CIOS Report of 16 August 1945).

Ethane and oxygen are preheated separately and mixed, whereby an incomplete combustion occurs, resulting in a flame. No catalyst is used. The reaction takes place at 1-2 m. of water pressure and a reaction temperature of 1300-1600°C. The exit gas contains about 9% of acetylene besides carbon oxides, hydrogen and unconverted hydrocarbon. The yield of acetylene is about 0.33 kg. per kg. of ethane.

V. POLYMERIZATION AND CONDENSATION PROCESSES.

A. Oppanol.B.

The following information on the preparation and properties of Oppanol was given by Dr. Güterbock and on applications, by Dr. Schwarz.

Oppanol is polyisobutylene, prepared by polymerizing isobutylene in the presence of ethylene to control the temperature at -100°C. and of about 0.05% of boron fluoride as catalyst. The isobutylene and ethylene (liquid ratio 1:2) with the boron fluoride are charged in liquid phase onto a concave endless belt. The ethylene evaporates as the polymerization progresses, maintaining the temperature at -100°C. The belt is inclosed in a case from which the vaporized ethylene is recovered for recycling. The boron trifluoride (prepared from CaF_2, B_2O_3 and H_2SO_4) leaves the reactor with the ethylene and is removed from it by contacting with CaO. The polymerized product is scraped from the belt into a heated kneader, where the last traces of ethylene are evaporated.

The belt is made of V2A steel; the case and other equipment, of iron.

The ethylene and isobutylene must be of the highest purity obtainable (99.5 + %). The isobutylene is prepared by the dehydration of isobutanol at 400°C under atmospheric pressure with an aluminagel catalyst.

Products of various molecular weights are obtained by adding polymerization "poison"; the best results were obtained with diisobutylene. The commercial grades were as follows:-

B3	3,000 mol. wt.
B15	15,000 "
B50	50,000 "
B100	100,000 "
B200	200,000 "

Properties of B-15 are:

Sp. gr.	0.9
Ignition Point	Very high
M.P.	Not definite, thermoplastic.
Neutralization No.	Neutral

The applications of these products were as follows:

a) Oppanol B3

Cable oil, lubricating oil, softeners for resins and waxes, etc.

b) Oppanol B15

Viscosity improver for lube oil and cable oil. Additive to bitumens, waxes, paraffin, etc. Softener for polyethylene, gutta percha, and similar resins.

c) Oppenol B50, B100 and B200.

Foils for electrical insulation and protection against corrosion. Gaskets for chemical containers and grooved-can joints. Combination with polystyrene and polyethylene for electrical insulation for high-frequency cable casing and packing: Combination with polyethylene for submarine cable. Adhesive plasters and adhesive tape. Combination with wax, paraffin etc. for doubled steam-impermeable paper. Covering materials of all kinds in liquid form, with special stability against aging and chemicals. Blending with bitumens to increase viscosity and "dripping point". Mixed with natural and synthetic rubber for special applications.

B. Isobutylene Dimerization.

The following information was obtained from Dr. Kuhn:

Isobutylene is passed in the liquid phase at a space velocity of 3 to 5 liters per liter catalyst per hour over phosphoric acid on activated charcoal as catalyst. Conditions: 180-200°C., 25 atm. gage pressure. Thirty to fifty percent of this isobutylene polymerizes per pass, the remainder, after distillation, is recycled. Diisobutylene is the desired product but triisobutylene cannot be avoided. One liter of catalyst can produce one to two cubic meters of product. Isobutylene as pure as possible is used to avoid losses in (pressure?) vent-release in the recycle system. Construction material is iron. The yield is practically 100 percent if the equipment is gas tight. There are no byproducts, excepting 0.1-0.5 percent of tetraisobutylene which is separated by distillation. The product is a mixture of diisobutylene and triisobutylene, which is hydrogenated to "Tannol". The product is tested for octane number and distillation range.

C. Lupolen H.

The following information on the preparation of Lupolen was obtained from Dr. Heinrich Hopff, and on the properties, from Dr.Schwarz.

The process is carried out at a pressure at 1500-2000 atm., using 0.05-0.10 percent of oxygen as catalyst. The reaction starts at 220°C. and temperature is controlled between 180 and 220°C. by cooling. The apparatus, as shown in Fig. VI, consists of (a) a first-stage compressor to 300 atm., (b) a high pressure compressor to 1500-2000 atm., (c) a pipe coil 24 mm. diameter and 80 m. long, 40-50 l. volume, (d) a separator, and (e) a caustic washer. Heating and cooling are done by water under pressure at 200-220°C. in the first section of the coil, and 100-120°C. in the second section. The conversion to polymerization products is 8 to 10 percent per pass. Monthly production is 5 tons.

The etylene feed is 98-99% ethylene, about 1% ethane, about 0.5% nitrogen and a trace of acetylene.

The viscous Lupolen H is drained into a tub and after cooling it becomes a snow-white mass. The product contains 0.2 to 0.3 percent of oxygen. Testing is done by milling a thin sheet on heated rolls and determining the stress, crease number (Knitterzahl) and dielectric-loss angle. In addition the molecular weight which should be between 15,000 and 25,000 is determined in boiling tetralin by the method of Staudinger.

Lupolen H is a horny, tough material of paraffin-like character, tasteless and odorless, waterproof, heat-proof up to about 100°C., stable against chemicals, and with good dielectric properties. It is used alone or with Oppanol B as electrical insulating material, including use in submarine cable, as a low-loss insulation in high-frequency work, also as a cable-covering material.

It is also used alone or with Oppanol B. for acid-proof covers, packing, etc., and for taste-and odor-free wrappings of all kinds.

D. Paraflow.

The following information concerning the preparation of Paraflow was obtained from Dr. Fritz Christmann.

Hard paraffin, 1000 kg., 50-52° C M.P., is chlorinated to 12-14 percent chlorine by the addition of gaseous chlorine at a temperature of 80°C. It is then diluted in a stirred vessel with about 1000 kg of ethylene chloride. After cooling to 20°C., 150 kg. of naphthalene, 10 kg. of polystyrene and 35 kg. of zinc oxide are added. Gradually, over 12 hours, 70 kg. of $AlCl_3$ is added, with stirring. In this period, the reaction temperature rises slowly to 30 to 35°C. After an additional 24 hours, the reaction temperature reaches 60°C., after which the reaction product is centrifuged to remove insoluble salts.

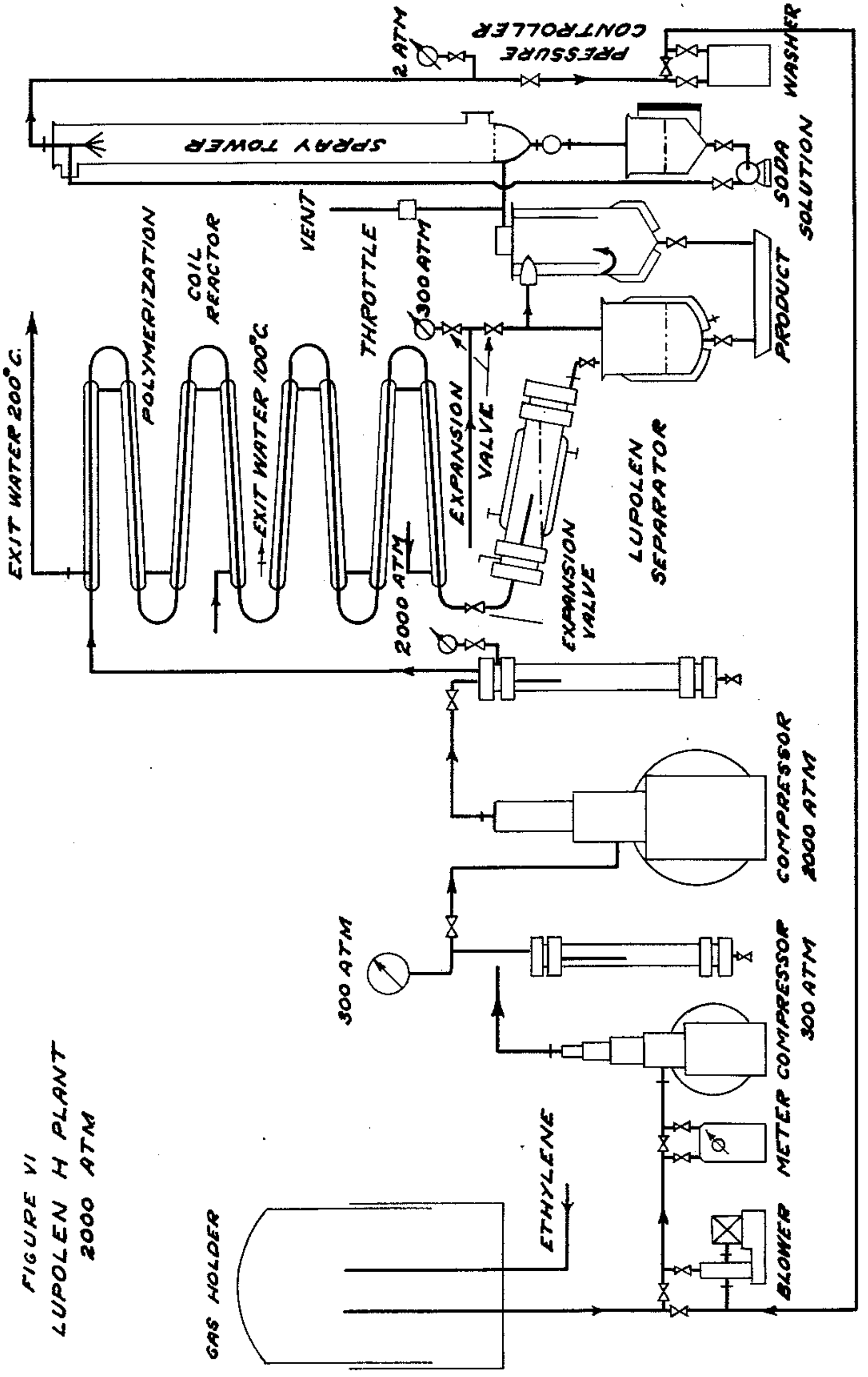

FIGURE VI
LUPOLEN H PLANT
2000 ATM

The centrifuged product is then treated with 30 kg. of fuller's earth (Terrane) in a gas-heated agitator, during which time (12 hours) the temperature is raised to 240-270°C. The ethylene chloride is distilled off in the process and is replaced with kerosene. The product is cooled to 100°C. and filtered. The filter cake is twice extracted with kerosene. The filtrates are combined and vacuum-steam distilled in a pipe still, where kerosene and a paraffin-containing spindle oil are recovered as overhead products. The residue of 650 kg. (65% of original paraffin) is Paraflow fluid with a viscosity of 50-80°E. at 100°C, which is mixed with other oils (motor oils, spindle oils) in a ratio of 10:90 and sold as Paraflow.

The Ludwigshafen Paraflow plant has a capacity of about 20 T/Month Paraflow Fluid (= 200 T/Mo commercial Paraflow). The plant is practically intact and can reach this capacity in a few months.

E. Bunol.

The following information was obtained from Dr. Steinhofer on the preparation of Bunol, which is a butadiene polymer, claimed to be a suitable substitute for drying oil, such as linseed oil.

Butadiene is introduced with stirring into a suspension of two parts of potassium sodium alloy in 400 parts of toluene at 90°C. The reaction takes place violently, the temperature rising to 170°C. so that the toluene boils under reflux. After 8 to 10 hours, the reaction subsides. About 8000 parts of oil are formed; half is taken off and filtered. The other half, remaining in the kettle, is mixed anew with 200 parts of toluene and can be used again for the reaction without the addition of catalyst.

Details could not be furnished since the process was carried out at Schkopau, and due to lack of communications, the information was not available.

F. Buna D.

The following statement concerning Buna D was obtained from Dr. Herbeck.

Buna D is a co-polymer of butadiene and Dimol. Dimol is ethylidene dimethylvinylcarbonol, and is made by the addition of vinyl acetylene to acetone.

The product is polymerized in emulsion by customary methods and its qualities are about the same as those of Buna S.

G. Production of Koresin.

The following brief information was obtained from Dr. Christ on Koresin Preparation:

Koresin is prepared by treating a mixture of p-tert butylphenol (distilled product) and 8% zinc naphthenate ("Solingenzink") in a stirred autoclave with a mixture of acetylene and nitrogen until 1.3 to 1.5 mols of acetylene have reacted with 1 mol of the butylphenol. Operating conditions are 200-240°C, 20 atm. total pressure, 3 atm. partial pressure of nitrogen. The reaction product is forced by pressure to another agitator at 200°C., and from this vessel is emptied at 180-200°C. into wooden barrels or paper bags. It sets to a brittle brown resin of 120-130°C. melting point, corresponding to a dripping point of 130-140°C. by the method of Kramer and Sarnow.

Report No. 241, Dr. Hecht, May 25, 1940, "Koresin" is available through CIOS, CAFT III.

VI. CHLORINATION PROCESSES.

A. Preparation of Alkyl Dichlorides.

The following information was obtained from Dr. Leutner:

The chlorination of propane to dichlorides is carried out by mixing liquid propane and liquid chlorine in equimolar amounts in the presence of propylchloride, ten times the equivalent of the chlorine. This mixture is precooled and exposed to a mercury-arc lamp, in several stages. Intermediate cooling takes place between the stages so that the temperature does not exceed 70°C. The pressure has to be sufficient to maintain the liquid phase and insure solution of the hydrogen chloride formed. The process may be carried out batchwise or continuously by recycling the products through the coolers and exposure stages, removing product equivalent to the fresh feed.

The products are separated, by distillation, into hydrogen chloride, propane, propyl chloride, propyl dichloride (50% of 1,3 dichloropropane) and a small residue of higher chlorinated products. The propane is mixed with fresh propane and returns to the process with the propylchloride. The yield of propane dichloride is about 99% of theory.

Butane dichloride can be produced in a similar manner. In this process, the temperature must not exceed 40-50°C. A pressure of 15 atm. is required. A yield of almost 100% is realized, including some trichlorobutane.

B. Preparation of Butadiene from Butylene.

This information on the production of butadiene from butylene was obtained from Dr. Leutner:

The chlorination of butylene is carried out in a high-speed centrifugal pump by introducing gaseous chlorine into a mixture of liquid butylene and an excess of dichlorobutane. In order to obtain an immediate reaction with the butylene, the chlorine is introduced axially into the pump through a nozzle. At a pressure of 4-6 atm. the circulating mixture is maintained in the liquid

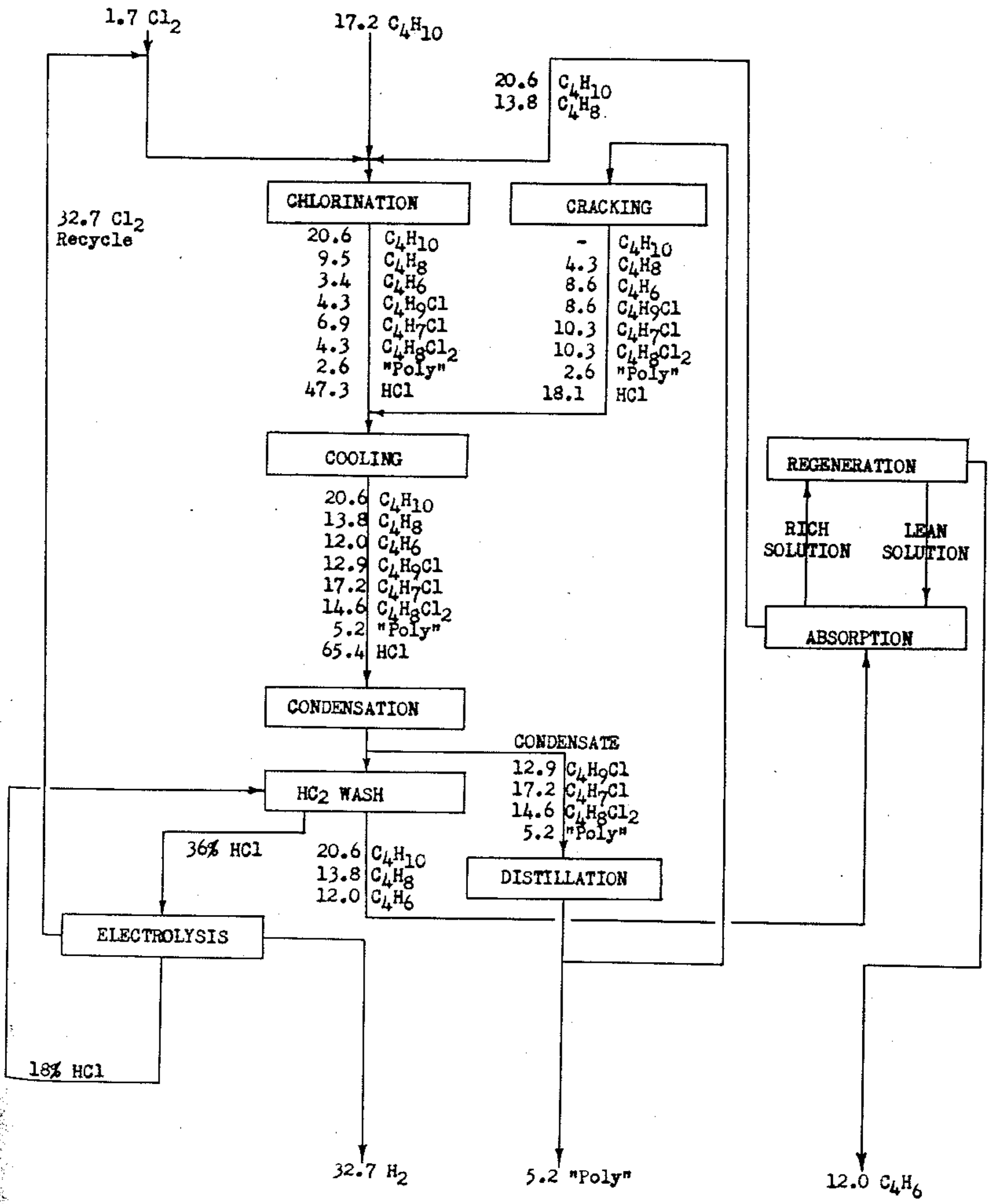

Fig. VII FLOW SCHEME FOR BUTADIENE PRODUCTION