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SYNTHETIC RUBBER PLANT
CHEMISCHE WERKE—HULS

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[1945]

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PART I - GENERAL.

SUMMARY.

Chemische Werke, Hüls represents the latest and most modern design of German Buna S synthetic rubber operations. The plant has a rated capacity of 4000 tons per month of Buna S. Production at this rate was obtained during the early part of 1944 when operations were essentially uninterrupted by war conditions. During the last quarter of 1944 and first quarter of 1945, production was reduced to approximately 35% of rated capacity because of severe bomb damage to the nearby synthetic oil plants which supplied Hüls with its major requirements of hydrocarbon gases for acetylene manufacture.

At the present time, the plant is in excellent condition with the exception of minor bomb damage to several units sustained just prior to occupation of the area by Allied Forces. It is estimated that the plant could be returned to full operation within two to three months provided that it were supplied with the necessary raw materials.

Hüls is the only plant in Germany which manufactures acetylene by the electric arc cracking of hydrocarbon gases. Acetylene is converted to acetaldehyde and butadiene is produced from the latter by the so-called aldol process. For styrene production, benzene is obtained from coal tar plants in the Ruhr and ethylene is produced at Hüls. Butadiene and styrene are polymerized continuously in emulsion to Buna S. Four types of Buna S have been produced at Hüls: Buna S, Buna SS, Buna SR, and Buna S3. Related organic chemicals including rubber softeners are also manufactured.

Details of the butadiene, styrene, and polymerization processes were obtained.

PART I GENERAL

Target:

Chemische Werke Hüls G.M.B.H.
Hüls K52/A54 ; part of the
village of Marl, Kreis Recklinghausen

CIOS Black list target No. 22/6

Team:

E.T. Handley, U.S.A., T.I.I.C., Leader
C.C. Monrad, U.S.A., T.I.I.C.
B.S. Garvey, U.S.A., T.I.I.C.
N.R. Rowzee, Canada, Ministry of Supply
R.D. Juve, U.S.A., T.I.I.C.
J.E. Troyan, U.S.A., T.I.I.C.
~~J.D. Fennebresque, U.S.A., T.I.I.C.~~

Itinerary of Team.

Messrs. Monrad, Rowzee, Juve, Troyan, and Fennebresque left London April 17, 1945, by special plane and flew directly to Krefeld, Germany. The next morning, April 18, they proceeded by truck to T Force Headquarters at Herten (Kreis Recklinghausen), and arrived at the target the early afternoon of the same day. The balance of that day was spent in obtaining an overall view of the plant operations.

Mr. Fennebresque, previously had spent the week of April 1 to 7 at the target for the purpose of assessment and preliminary investigation under the auspices of C.A.F.T. He left this target the morning of April 20 to assess Leverkusen (22/2) on C.A.F.T. assignment.

Mr. Handley left from Paris by truck, the morning of April 17, arriving that evening at Verdun (12th Army Group Headquarters). Dr. Garvey arrived at Verdun the same afternoon, having come from Frankfurt by truck. Messrs. Handley and Garvey then proceeded by truck from Verdun the morning of April 18, spending that night at Krefeld and arriving at the target at noon of the next day (April 19).

The team remained at the plant through April 23, at which time Mr. Fennebresque rejoined them. On the morning of April 24, they proceeded to Leverkusen (22/2) Messrs. Handley, Garvey, Rowzee, and Juve remained at Leverkusen for investigation of that target, and Messrs. Monrad, Fennebresque and Troyan left on the morning of April 25 for investigation of Schkopau (22/82).

Plant Personnel.

The two managing directors, Dr. Ulrich Hoffmann, and Dr. Hans Günther had left the area just prior to occupation by American troops. Dr. Paul Baumann, deputy managing director, had been left behind and had taken over all managerial duties. Under the organization plan, he was also director of the technical division which included production, research, and development. During 1930-1935, Dr. Baumann had been in the United States as liaison officer for I.G. Farbenindustrie with Standard Oil Development Co. Consequently, he speaks English fluently. Dr. Beckman, in charge of engineering, who is the fourth director of the company, was also available. A complete organization plan for the company was found and included in the documents removed.

The following key personnel were interrogated by the investigating team, in addition to those previously mentioned: Drs. Zobel, Haberl, and Weichert, acetylene manufacture and gas separation; Drs. Bub, Haag, Frank, and Saurwein, aldoling, hydrogenation, and butadiene manufacture; Drs. Roh, Hillemann, and Brunotte, ethylbenzene and styrene manufacture; Drs. Meis, Knoche, Wollthan, Hormuth, Rosenberg, and Schneider, Buna operations including production, rubber testings, and pilot plant.

Documents:

Apparently no important technical documents had been removed from the plant prior to occupation by American troops. The managing directors, Drs. Hoffmann and Günther, were known to have taken some secret data and files primarily of a financial nature with them at the time of their flight from the area.

The investigating team removed three CIOS bags of documents from the plant and delivered them to T-Force Headquarters for transmittal through proper channels to the C.I.O.S. Secretariat in London. These documents include: process and research reports; production; cost and yield data; minutes of I.G. Farbenindustrie rubber technical committee meetings; engineering drawings of important equipment items; drawings of plant layout, etc. In addition, the investigators requested Dr. Baumann and his staff to prepare process descriptions and schematic flow sheets of all operations relating to Buna production. A complete list and explanation of all documents removed can be found in the appendix.

Two hundred kilograms of catalyst used for dehydrogenation of ethylbenzene to styrene was obtained for testing by the Allies in comparison with currently used materials.

General Description of Plant.

Chemische Werke Hüls is controlled and operated under the direction of I.G. Farbenindustrie. The plant is valued at 500,000,000 RM. It was primarily designed for the production of Buna-S type synthetic rubbers, having a rated capacity of 4000 metric tons per month, making it the second ~~largest Buna plant in Germany. It is self-~~ sufficient from the standpoint of producing its own requirements of Butadiene and styrene. Acetylene for the manufacture of butadiene by the well known aldol process is produced by the electric arc cracking of hydrocarbon gases. For styrene production, benzene is obtained from coal tar plants in the Ruhr, and ethylene is produced at Hüls. Related organic chemicals including rubber softeners are also manufactured.

Construction of this plant was commenced in 1938 and put into operation in August, 1940. The plant operated until March 29, 1945, the day prior to occupation of the area by troops of the U.S. 9th Army. The plant site covers an area of approximately ¾ square miles. The main gate is at the south end and the manufacturing buildings are arranged in blocks running east and west, and north and south, and numbered accordingly. The administration office is located on the right in the first block after entering the south gate and is numbered 139. The main research building, No. 141, is directly west of the administration building. Railroad switching yards are along the east side of the plant. A barge canal borders the north side with dock unloading facilities at the northeast corner.

The power plant has a rated capacity of 125,000 KW., and a maximum capacity of 175,000 KW. It represents the most modern power plant design in Germany. High pressure steam at 125 atmospheres is produced. Low pressure steam from the primary turbines, and condensate from the secondary turbines are available for chemical processing.

Mercury arc rectifiers are used for converting to D.C. current where required. The power plant is tied into the R.E.W. and V.E.W. systems for the north Ruhr area. The major coal requirements are supplied by the Zeche Auguste Viktoria A.G., a coal mine approximately two miles south east of the plant. There is also a small colliery adjacent to the plant on the east side.

For full operation, the plant required a total personnel of 7000 employees, of which 1000 were foreign workers during the last three years. 2000 employees were involved in maintenance and construction operations. 95 PhD. chemists, and 150 mechanical engineers were employed.

The butadiene, styrene, and polymerization operations at Hüls represented improvements over the design of the Schkopau plant which was the first Buna-S type synthetic rubber plant in Germany to be put into production. It is evident that the Hüls management was allowed considerably more latitude in process research and improvements than at Schkopau.

The bottleneck in increasing production of Buna was in the equipment for acetylene manufacture and gas separation. Consequently, plans were made and construction started in 1942 for the expansion of that part of the plant. This work was subsequently halted because of inability to obtain high pressure compressors required in gas separation and purification.

Condition of Plant and Effect of Bombing.

The plant is essentially in good operating condition. Some minor damage to facilities was done by fighter-bomber attacks during the two weeks prior to occupation of the area. The unit for production of the catalyst for butylene glycol dehydration was partially destroyed, but it was estimated by the plant management that it could be repaired in two to three months. Other damage is limited to certain manufacturing units, warehouses, railroad sidings, and overhead process lines. A short review of the damage to units involved in the Buna operations is included in the appendix. The power plant suffered no damage. If the plant were supplied with its requirements of raw hydrocarbon gases, benzol and other miscellaneous raw material chemicals, it is estimated that full production could be resumed in two to three months. There is on hand a normal inventory of in-process intermediates.

The only major bombing raid on the plant was a daylight attack on June 22, 1943. This resulted in a direct hit on the main acetylene gas holder which exploded and did considerable damage, particularly to the facilities for manufacturing acetylene. The plant was shut down entirely for two months. By that time repairs had progressed so that partial operations could be carried out by having acetaldehyde shipped in from the Knapsack plant. Repairs were continued on that part of the plant for producing acetylene, and six months after the raid, the plant was returned to full operation.

Production gradually declined during the last two quarters of 1944 and the first quarter of 1945 because of the effect of bombing on the two plants supplying the major portion of the raw hydrocarbon gases - Gelsenberg Bergin A.G., at Gelsenkirchen, and the Hydrierwerk Scholven A.G., at Scholven. Following very heavy air raids, these two plants were unable to deliver any gases to Hüls after October, 1944. Thereafter, the primary source of gas was from the Bentheim natural gas wells, which, however, was limited to approximately 35% of Hüls normal requirements. (Refer to Buna S production data in appendix.)

Outline of Operations.

Unlike the other synthetic rubber plants in Germany, acetylene was produced at Hüls by the electric arc cracking of hydrocarbon gases (methane and/or methane-ethane mixtures). The primary sources of the gases were from the two nearby coal hydrogenation plants at Gelsenkirchen and Scholven. The total gas requirement for capacity operation was 130,000 to 140,000 metric tons per year, obtained as follows:

Scholven	... ...50,000 tons/yr
Gelsenkirchen	... ...50,000 " "
Zeche Auguste Viktoria	... ...15/20,000 " "
Zweckel	... ...15/20,000 " "

The gas from Auguste Viktoria is by-product from coke oven operations. At Zweckel, there is a plant for manufacture of ethylene oxide. For this operation, by-product coke oven gases are obtained from Scholven, the ethylene is fractionated off and the remaining saturated hydrocarbon gases are delivered to Hüls.

Approximately two years ago, Hüls contracted with the Bentheim natural gas wells to deliver up to 50,000 tons per year. This was contracted for in anticipation of the plant expansion referred to previously. No gas was obtained from this source until Gelsenkirchen and Scholven were unable to deliver because of bomb damage. Thereafter, the full contract quantity was taken.

The n number of the gases from Gelsenkirchen and Scholven varied from 1.1 to 1.5 (10% ethane to 50% ethane). The n number for the natural gas from Bentheim was .95 (essentially 100% methane).

There are 15 sets of arcs with mercury rectifiers. Each set has 2 arcs, one being in operation at the time. The arc operates at 1000 volts with a power consumption of 7000 KWH for a gas input of 2800 cu.metres hr. The reaction takes place in a 1 meter long, water cooled, jacketed steel tube. The terminal temperature of the gas in the tube is 1600°C, which is cooled immediately to 150°C by a water spray. The conversion of the gas to acetylene is approximately 50% per pass, with an overall weight yield of 45 to 50%. Unreacted hydrocarbon gases are recycled through the arc system after separation. (Linde plant). The power requirement of the arc per metric ton of acetylene is 9,500 to 10,000 KWH, which is comparable to that required by the calcium carbide process. The average cost of purified acetylene by the arc process was 30 RM per 100 kg. based on a power cost of .015 RM per KWH and a gas cost from the coal hydrogenation plants of 1.5 RM per 1,000,000 B.T.U.

From the arc reaction there is produced carbon black which is removed from the product gases by cyclones and water scrubbers. The yield of carbon black is 5 to 6% which is equivalent to a monthly production of 500 tons, and is shipped to tire manufacturers. Acetylene is removed from the reaction gases by absorption in water at 18 atmospheres and is then stripped off at 96-97% purity. Some ethylene is also produced from the arc reaction; the yield of ethylene increasing with an increase in the n number of the feed gases. Ethylene, hydrogen, and unreacted methane and ethane are separated from each other by low temperature distillation (Linde plant). The hydrogen required for the hydrogenation of aldol to butylene glycol in the butadiene process, is purified by low temperature distillation (-180°C) using liquid nitrogen as reflux. By this operation it is possible to obtain hydrogen with a CO content of less than .0001.

Process nitrogen for blanketing is obtained by liquefaction of air. The liquid oxygen was shipped to the steel plants in the Ruhr area for welding. During the last year of operation, Hüls supplied the Scholven and Gelsenkirchen plants with nitrogen as their Linde plant had been destroyed by bombing.

The ethylene requirements are supplied from four sources as follows: by-product from the electric arc, ~~hydrogenation of acetylene, dehydration of ethyl alcohol,~~ and coke oven gas separation at the Zeche Auguste Viktoria. The major portion of ethylene is produced by the hydrogenation of acetylene using palladium on silica gel as catalyst, a reaction temperature of 200°C, and 100% excess hydrogen. Ethane and butane are by-products in small quantity (5 to 10%). 600 tons per month of ethylene were produced by this process, and are used primarily for ethylation of benzene in the styrene operations. Large quantities of ethylene are also manufactured by the dehydration of ethyl alcohol (potato) using CaO as catalyst. However, because of inadequate distillation equipment for the removal of by-product ethers, the ethylene could not be used for benzene ethylation, but was suitable for the manufacture of ethylene oxide.

Acetylene is converted to acetaldehyde by passing the gas up through a mercury-sulfuric acid catalyst in the presence of ferric sulfate.

Butadiene is manufactured from acetaldehyde using the so-called aldol process. Acetaldehyde is condensed to aldol in the presence of KOH. Aldol is hydrogenated to butylene glycol at 300 and 700 atmospheres, over a chromium activated copper catalyst. Butylene glycol is dehydrated to butadiene at 280°C using a phosphate catalyst deposited on coke. The yield on the dehydration step is 82% of theory and the yield from acetaldehyde is 65%. Utilized by-products from the butadiene process are: crotonaldehyde, butanol, ethanol, 2-ethyl hexanol, and hexantriol. The hexantriol was sold to lacquer manufacturers where it is condensed with phthalic anhydride for use as a glyptol type resin.

The styrene process is a two step operation: ethylene and purified benzene are reacted at 90°C in the presence of $AlCl_3$ catalyst to form ethylbenzene, and the latter is dehydrogenated in the presence of steam to styrene at 600°C using a zinc oxide base catalyst. Some diethylbenzene was shipped out for use in aviation gasoline stocks. The still bottom residue, from the ethylbenzene distillation, boiling higher than hexaethylbenzene was sold as Plasticator R.A., a softener used in tyre manufacture.

Butadiene and styrene are polymerized in emulsion continuously, with each line consisting of six reactors in series. Hüls was the only synthetic rubber plant in Germany to produce all four types of Buna S used on a commercial scale: Buna S, Buna S-3, Buna SR, and Buna SS. Ludwigshafen and Schkopau produced Buna S and S-3 only. Buna S was the original butadiene-styrene rubber in which linolein acid was used as a polymerization regulator.

~~However, because of critical shortage of~~ linseed oil which developed during the early part of 1944, it was necessary to switch to the manufacture of Buna S-3 which used diisopropylxanthagen disulfide as the regulator. Buna SR is a 50-50 mixture of Buna S and Buna R, the latter being a high conversion Buna S carried out at high temperature during the last stage of the polymerization. Buna SS is the high styrene content rubber used for extruded articles because of its easy processing. The production of Buna showing the breakdown by types is given in a table in the appendix. It will be noticed that during the first quarter of 1944, the plant produced at the rated capacity of 4000 tons per month.

Coagulation of the latex was originally done using brine and acetic acid. However in 1944, there developed a shortage of acetic acid because of bomb damage to the Knapsack plant. At that time sodium bisulfite was substituted for acetic acid. In late 1944, a unit was in~~stalled at Hüls for the manufacture of the sodium bisulfite.~~ H_2S obtained from scrubbing of the by-product coke oven gas is oxidized to SO_2 and the latter is absorbed in NaOH solution to form $NaHSO_3$

The coagulated rubber is formed into sheets and washed on Fourdrinier machines. Drying of the rubber sheet is done continuously at 110°C.

The emulsifier for the polymerization, Nekal, which is diisobutyl sodium naphthalene sulfonate, is manufactured at the plant from butanol, caustic, sulfuric acid, and naphthalene.

Several months ago, approximately 20 tons of Buna N was produced at Hüls because of bombing damage to the Buna N polymerization unit at Leverkusen. For the purpose, acrylonitrile was shipped from Leverkusen. Normally, Hüls supplied Leverkusen with its requirements of butadiene and also styrene for special experimental types of polymers. Leverkusen was rated at 800 tons per month of Buna.

Ethylene oxide is produced from ethylene through ethylene chlorhydrin, by the conventional process. The ethylene oxide unit has a capacity of 1600 tons per month. Ethylene chloride is a by-product (approximately 15%) in the ethylene oxide process. Chlorine is produced by electrolysis of brine using mercury cells. The unit has a rated capacity of 2500 tons per month of chlorine.

Glycol and diglycol are manufactured from ethylene oxide in caustic solution at 200°C and at 16 to 40 atmospheres pressure. The reaction can be preferentially controlled to give primarily diglycol by operating at the higher range in pressure and recycling glycol. Diglycol was shipped to the interior of Germany for nitration, and this product used as a substitute for nitroglycerine. Glycol was used as an antifreezing agent. The plant normally operated to produce 1200 tons/month of diglycol and 600 tons per month of glycol. A small amount of triglycol is a by-product from this process and was used as a hydraulic fluid.

Ethylbenzene is oxidized in the liquid phase using a copper catalyst to acetophenone. It was originally intended to use the output of this unit for the production of chloracetophenone (chlorine substituted on the methyl group) for use as a chemical warfare product said to be effective in clogging the active carbon in gas masks. However, before the unit came into operation the intended use was discarded, and thereafter the output was used for condensing with formaldehyde. This is known as Resin A.P. and is used in the manufacture of lacquer. Sodium benzoate is a by-product in the oxidation of ethylbenzene.

Distyrene (dimer) is produced by condensing styrene in the presence of sulfuric acid. 10 to 20 tons per month of this product was manufactured and sold as a rubber softener in tire manufacturing.

The most recent technical development at Hüls was a process for the manufacture of Softener 111, which during the last few months was one of the main rubber softeners used in tire manufacture. A unit for producing 70 tons/month was put into operation in December 1944. The process is as follows: Aldol is converted to crotonaldehyde by high temperature distillation and then to crotonic acid by oxidation at 20°C using a copper-manganese catalyst. Some crotonaldehyde is also obtained as a by-product in the butadiene operations, and is utilized in this process. The yield on the oxidation is approximately 80 to 90% crotonic acid and 10-20% acetic acid. The mixture is esterified with butanol which is also a by-product from the butadiene process. Butyl acetate is separated by distillation and sold as a solvent. The butyl crotonate is reacted with H_2S, the S acting as the linkage of two mols of the ester at the double bonds.

The Hüls plant apparently had been permitted to carry on considerable process research and development work. There are extensive facilities for research in glass equipment as well as a small pilot plant for polymerization and high pressure reactions. A research program had been instituted, directed towards the utilization of by-products from the plant's operations.

This resulted in work having been done on acetylene, diacetylene, and acetaldehyde chemistry. Some limited research had been started on the Lebedev process for the manufacture of butadiene from alcohol in one step.

PART II - TECHNICAL.

MONOMER PREPARATION.

The main raw materials required for the production of Buna S rubbers are butadiene and styrene. The butadiene is made at Huls by the well-known aldol process starting from acetylene from arc cracking of hydrocarbons, conversion of this to acetaldehyde, then to aldol, 1,3 butylene glycol and butadiene. The styrene is made by alkylating benzene and ethylene to form ethylbenzene and dehydrogenating the latter to styrene.

One of the most important items to consider in evaluating the processes used for manufacturing these materials is the yield obtained on each step compared with theory. Consideration must also be given, of course to the value of any by-products made particularly where these may be recycled to improve yields. In general it was found that the Germans obtained reasonably good yields on all steps except in the dehydration of 1,3 butylene glycol to butadiene. In this step up to 10% allylcarbinol is produced which is recycled to the reactors and hence is not a net product. However, the other by-products which could not be converted to butadiene were quite large. Considerable effort was made to use all the by-products from the various steps for solvents, ersatz plastics and plasticizing agents, etc.

The following tabulation shows a summary of yields on each step compared with theory, as obtained from discussions, and as derived from 1944 actual plant records.

Styrene manufacture.	From Discussions	From 1944 records
Ethylene to ethylbenzene	93%	94.5 %
Benzene to ethylbenzene	94%	
Ethylbenzene to styrene	90%	90.2 %
Overall benzene to styrene	85%	85 "

Butadiene manufacture.	From Discussions	From 1944 records.
Acetylene to acetaldehyde	94 %	91.7 %
Acetaldehyde to aldol	88 %	99.1*%
Aldol to 1,3 butylene glycol	94 %	98.9*%
Butylene glycol purification	98 %	81.9*%
Butylene glycol to butadiene	81 %	80.6 %
Overall acetylene to butadiene	62 %	60 %
Overall acetaldehyde to butadiene	66 %	65 %

* These figures are rather meaningless except as a whole since the intermediate products are not pure.

ACETYLENE PRODUCTION AND PURIFICATION.

Summary.

Acetylene is produced at Hüls by the electric arc cracking of hydrocarbon gases. There are two primary sources of hydrocarbons, by product gases from hydrogenation of coal consisting of methane-ethane mixtures, and natural gas from the Bentheim wells which is primarily methane. The arc operates at 1.5 atm, 1000 volts direct current, a reaction tube terminal temperature of 1600°C, and requires 7000 KW for a gas input of 2800 m^3/hr. Conversion per pass is 50% and the ultimate yield is 45% acetylene, 5 to 6% carbon black and 2 to 10% ethylene depending on the feed. Production per arc is approximately 15 tons of acetylene per day.

On leaving the reaction tube, the gases are quenched with water, carbon black is removed, and acetylene separated out by water absorption under pressure. The acetylene is purified to 97 to 98% concentration. Ethylene, hydrogen, methane, and ethane are separated by low temperature distillation (Linde unit). Methane and ethane are recycled to the arc.

Acetylene Production.

Acetylene is produced by the electric arc cracking of hydrocarbon gases using direct current at 7000 volts. The installation has 15 reactor sets, each set consisting of one mercury arc rectifier for converting alternating to direct current, and two arc-reaction tube units. Only one arc-reaction tube unit is on stream at the time, the other being held as standby. For rated plant capacity, 12 to 14 reactor sets were in continuous operation.

Figure 1 shows a cross sectional view of the arc-reaction tube unit. The high voltage lead to the primary electrode enters at the top (Hochspannungs-Anschluss). This electrode, made of copper, is jacketed for water cooling during operation, and insulated with porcelain. Feed gases enter tangentially (Gas-Zugang), circulating around in an annular space in the expanded head section of the unit, and pass through vertical slots to the arc zone at the center, and down into the reaction tube.

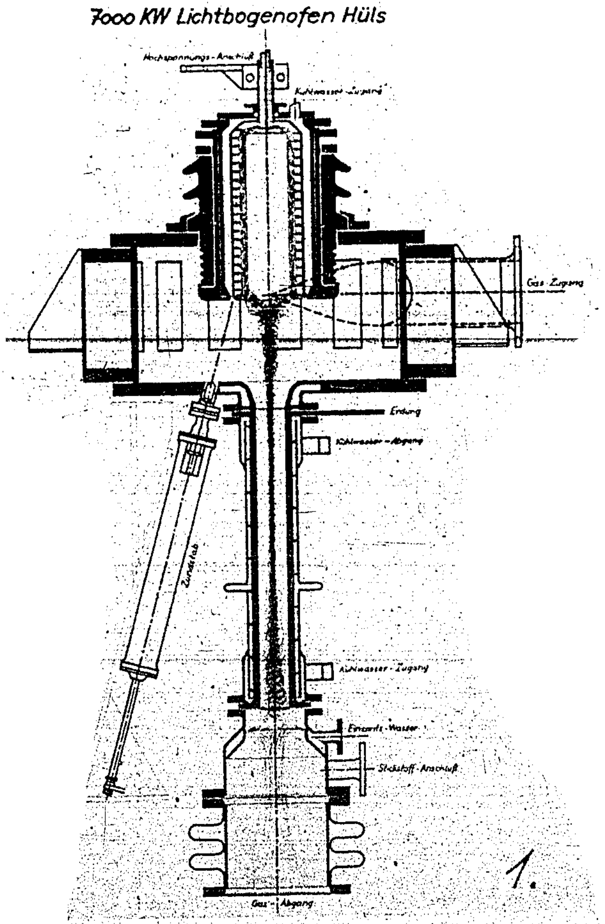


FIGURE I

ELECTRIC ARC FOR ACETYLENE MANUFACTURE.

This produces a high velocity swirling action to the gases and thereby eliminating burning out of the electrode and carbon deposition. The second electrode consists of a copper gasket at the head of the reaction tube and is grounded (Erdung). For starting up the arc, there is an auxiliary electrode (Zundstab) which operates by compressed air. In starting position, this electrode is up against the primary electrode. On formation of the spark, the expansion of the gases throws the auxiliary electrode back into position as shown in the figure, and simultaneously breaking its electric contact. The reaction tube is made of mild carbon steel, and is jacketed for water cooling (Kuhlwasser-Zugang and Kuhlwasser-Abgang). It is 1 meter long, 9.5 cm. inside diameter and has a wallthickness of 9.0 mm. The tube life is approximately 240 hours, and is replaced when burned out. A water spray (Einspritzwasser) enters into an expanded section just below the bottom of the reaction tube and immediately quenches the reaction gases.

The arc will operate with methane (Bentheim natural gas) or methane-ethane mixtures (by-product from coal hydrogenation) as feed The feed to the arc consists of approximately one part by volume of fresh gas and one part recycle. Each arc unit handles 2800 m^3/hr of feed which is expanded to 4200 m^3/hr during reaction. Operation of the arc is at 1.5 atm absolute. The terminal temperatures in the reaction tube is 1600° C. The reaction gases are then immediately quenched by a water spray (4 m^3/hr) to 150°. The primary electrode is jacket cooled with 8 m^3/hr of water and the reaction tube with 9 m^3/hr.

Typical volumetric analyses for the arc inlet and outlet gases with both types of feed are shown as follows:-

	*Refinery Gases		Natural Gas	
	Inlet Gas	Outlet Gas	Inlet Gas	Outlet Gas
CO_2	0.2	0.0	0.3	0.0
C_2H_2	2.7	16.2	1.5	13.3
Olefins	3.2	3.6	1.4	0.9
O_2	0.2	0.2	0.3	0.2
CO	1.4	1.0	3.0	2.9
H_2	10.9	50.5	2.5	46.0
CH_4 & hom	74.5	25.1	80.2	27.8
N_2	6.9	3.4	10.8	8.9
	100.0	100.0	100.0	100.0

Impurities in gm/m^3

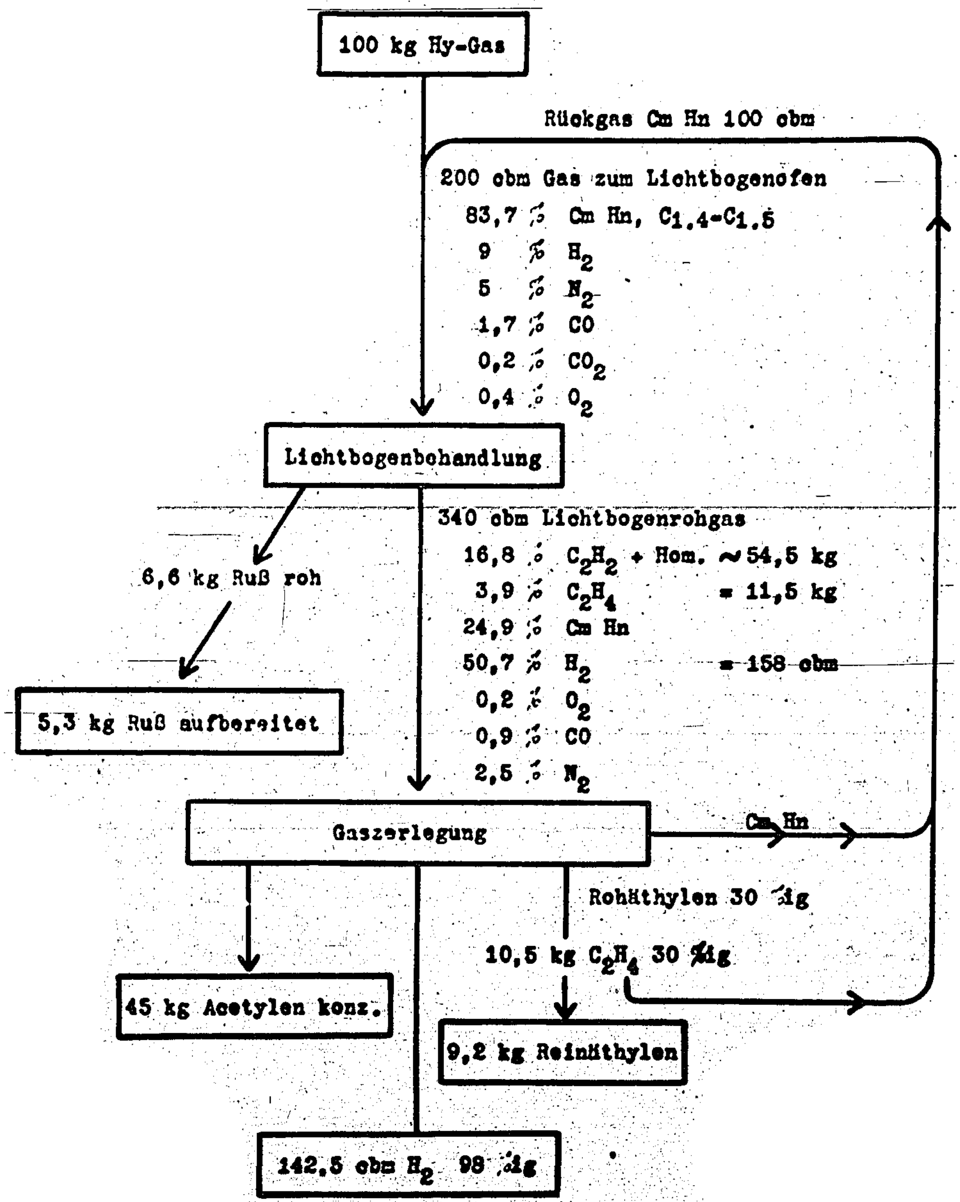
HCN	1-3	2-5
Naphthalene	1-3	0.12-2.0
Benzol	1-6	1.5-8.8
Diacetylene	15-30	15-30
H_2S	trace	trace
Carbon block	20-25	11

* By-product gases from coal hydrogenation for synthetic petroleum.

Conversion per pass through the arc is approximately 50%. Fig 2 shows a typical material balance around the arc system using by-product gases from coal hydrogenation, and feeding one part of fresh gas and one part of recycle. For 100 kg of fresh gas there is obtained 45 kg acetylene, 9.2 kg ethylene, 5.3 kg carbon black, and 143 m^3 hydrogen.

Referring to the previous table, it is calculated that for the same volume feed there is produced 606 m^3 acetylene and 61 m^3 ethylene from refinery gas, and 516 m^3 acetylene and 3 m^3 ethylene from natural gas. As the power consumption was indicated to be essentially independent of the feed type at constant volume throughput, it would appear that as the n number of the feed gas increases, the net production of both acetylene and ethylene increases per unit power consumption. The n number of the refinery gases varied from 1.1 to 1.5, and for natural gas averaged 0.95.

For a gas feed to the arc of 2800 m^3/hr and a resultant output of 4200 m^3/hr, the power requirement averaged 7000 KW. Referring again to the previous table, it is calculated that the power consumption in the arc per kg of acetylene produced is 9.93 KWH for refinery gas and 11.6 KWH for natural gas. This compares to 9.5 to 11.0 KWH per kg of acetylene by the carbide process using a figure for power consumption of 3.1 to 3.3 KWH per kg of carbide and a carbide requirement of 3.00 to 3.25 kg per kg of acetylene. These data are for actual conversion only and do not include auxiliary power for pumping, compression etc, which probably is higher for the arc process because of the involved purification system required.



F I G U R E 2.

Material balance around electric arc using by-product gases from coal hydrogenation.

Gas Purification.

After quenching the exit gas from the reaction tube to 150° C (dew point 92°), it is sent to two cyclones in series in which 60 to 70% of the total carbon black is knocked-down. The gas is sprayed with water in a wash tower to knock down most of the remaining black, and then passes through bag filters to remove the residual black. The bag filters are heated to prevent condensation. Most of the water carried in the gas is next removed by spray cooling with water at 20-25° bringing the temperature of the gas below the dew point.

Higher boiling constituents in the gas are removed by counter current washing with an aliphatic oil in a series of towers. The rich oil is stripped under 600 mm vacuum and recirculated. The gas from the oil washers is washed with water to remove HCN, and then passed through iron oxide boxes to remove sulfur.

After this preliminary purification, the gas is compressed to 19 atmospheres and absorbed in water in perforated plate towers. The non-absorbed gases consisting primarily of methane, ethane, ethylene, and hydrogen are passed to the Linde plant where ethylene and hydrogen are separated out and the paraffins are returned to the arc. Acetylene is stripped from the water by four stage flashing to a final pressure of .05 atm absolute. As the gas from the first stage is too low in acetylene (45%), it is recompressed and recycled through the absorber. The gas from the 2nd, 3rd, and 4th flashers is brought together as crude acetylene of 90% purity, and is further purified. Water from the last flasher is blown with residue gas from the Linde plant to remove last traces of hydrocarbon gases, which can then be returned as feed to the arc, and the water is sent to a cooling tower.

The crude acetylene is brought up to 97% concentration, with 1% CO_2 and 2% inerts as impurities, by a system of (1) low temperature condensation and evaporation using liquid ammonia, and (2) scrubbing with a petroleum distillate. This system removes the higher acetylenes (methyl acetylene, vinyl acetylene, diacetylene, etc). CO_2 is removed by scrubbing the acetylene with caustic solution giving a final purity of 97-98%. This acetylene can then be used directly for acetaldehyde and ethylene manufacture.

Linde Plant.

Hüls is equipped with a complete low temperature separation system for gases in order to prepare recycle gas for the arc system, and seperate ethylene, hydrogen, carbon monoxide, nitrogen and oxygen for use in the plant. Air is compressed to 130 atmospheres and separated into nitrogen and oxygen by low temperature fractionation. Non absorbed gases from the acetylene water absorber consisting of methane, ethane, hydrogen and ethylene, and by-product coke oven gas for use as feed to the arc, are separated into their components in low temperature distillation equipment using liquid nitrogen at 200 atm for cooling. Methane and ethane separated as a single fraction are sent to the arc for cracking. Hydrogen and carbon monoxide arc fractionated off and crude ethylene at a concentration of 15-25% is compressed to 30 atmospheres and purified to 95%, which is then suitable for ethylbenzene manufacture. Ethylene from hydrogenation of acetylene is also purified in this unit. The hydrogenation of the acetylene is carried out at 200° c, using palladium on silica gel as catalyst and 100% excess hydrogen.

PRODUCTION OF CARBON BLACK

AT

CHEMISCHE WERKE, HÜLS.

Summary

At Hüls two grades of carbon black are produced as by-products in the conversion of natural or refinery gas to acetylene. T. Russ is separated dry from the gas stream by cyclones and has a volatile content of 2-5%. N Russ is obtained by washing the rest of the black from the stream with water, filtering, and drying. It has a volatile content of 9-18%. Although not considered suitable for tire use the data ~~indicate that these blacks approach CK-3 in quality~~ and are fast curing.

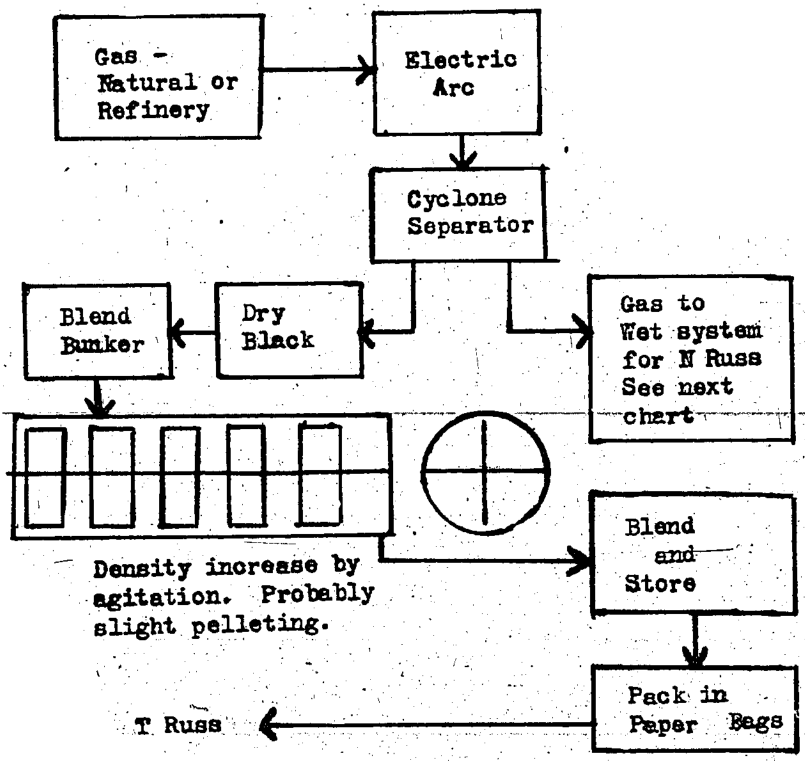
* * * * * * * *

Outline of Operations

The following diagrams show the essentials of the operation. More details of equipment and process are contained in Document No. Hüls 2925-104, "Betriebscheibung der Acetylenerzeugung einschliesslich Russfabrikation und Niederdruckgasreinigung" by Dr.Weichert.

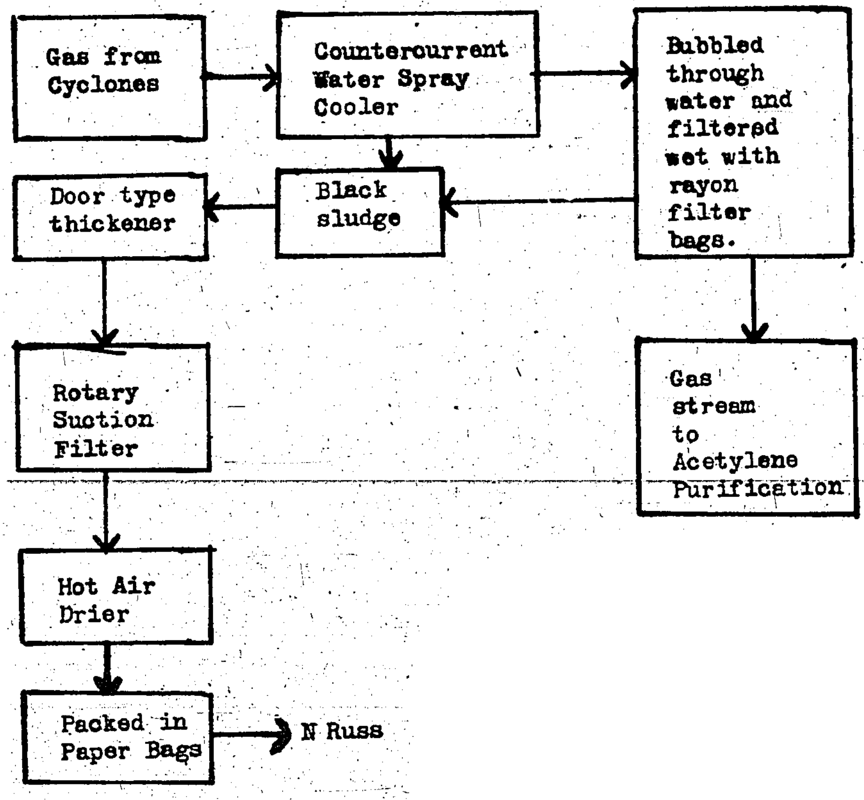
The starting product may be either natural gas or refinery gas or a mixture. With natural gas the ratio of T Russ to N Russ is 60% to 40% and with refinery gas 70% to 30%. The yields from refinery gas are approximately 7.5 g of T Russ and 3.5 g of N Russ per cubic meter of gas.

T - RUSS PRODUCTION



	Natural Gas	Refinery Gas
Volatile Matter	2-4%	3-5%
Production - Moto	200	400

N - RUSS PRODUCTION



	Natural Gas	Refinery Gas
Volatile Matter	9-11%	14-18%
Production - Moto	100	200

Quality of Black.

According to Drs. Bauman, Hormuth and Weichert, neither black has found use in tires. They are used in mechanical goods and were said to give stiff stocks.

From Dr. Hormuth's records the data in Table I comparing these two blacks with CK-3 black and with 1250 black have been selected as typical. These data are averages rather than specific test results. The data were taken for the cure of 60 min. at 274°F (134°C) on compounds mixed to the following recipe :

Buna S - Softened to Defo of 900	- 100
Kautschol	- 5
Stearic Acid	- 2
Zinc Oxide - Red Seal	- 5
Sulfur	- 1
Vulcacit AZ	- 0.8
Black	- 40.
	153.8

The scorch tests and shorter cures show that T-Russ is considerably faster curing than N-Russ which in turn is faster curing than CK-3. A better comparison would be obtained if the recipe were adjusted for rate of cure. However the figures as given indicate that both T-Russ and N-Russ are good blacks, approaching CK-3 in quality. The hardness is exceptionally high when compared to the other properties.

From the size of the installation it is apparent that the I. G. felt that these blacks showed considerable promise.

16. 5. 45.

BSG:ms

TABLE I

	Tensile Strength lbs/sq.in	Modulus at 300%	Elongation %	Hardness Shore	Rebound at 20°C
T Russ	2850	1425	475	74	44
N Russ	3000	1150	565	72	45
CK-3	3550	1300	560	66	51
P-1250	2200	775	600	66	45

ACETALDEHYDE PRODUCTION AND PURIFICATION.

Summary.

Acetaldehyde is produced by continuous hydration of acetylene in the presence of acid mercury and iron sulphate solution over metallic mercury. Conversion per pass is about 55% and the yield 93-95% of theory, the main losses being to byproducts with about 10% of the losses occurring in distillation. The product is recovered as a 7% solution of acetaldehyde and the latter purified by distillation to 99.9% purity. The mercury-iron sulfate solution is continuously renewed by oxidation of the ferrous iron to the ferric with nitric acid and by addition of fresh mercury. The reactor system, using 6 of the available 7 reactors will produce 360 T/day but the four distillation units limit capacity to 270 T/day. About 0.5 - 0.7% acetone (based on aldehyde) is recovered but diacetyl, crotonaldehyde and up to 2.0% acetic acid are wasted to the sewer. Mercury usage is about 0.1% based on acetaldehyde.

Acetaldehyde Production.

The production of acetaldehyde takes place in seven parallel systems of reactors. These reactors are vertical metal towers, lined with rubber, 1.3 m in diameter and about 15 m. high. Above the liquid withdrawal point the tower is 2.6 m in diameter and at the bottom the tower becomes a cone. Acetylene from the acetylene generation system and containing 97% C_2H_2, 1% CO_2, 2% N_2 and hydrocarbons is mixed with recycle acetylene of 75% purity from the reactors at a pressure of about 1.2 atm gage. About 1500 m^3 of fresh acetylene, and 1300 m^3 of recycle per hour is used per reactor making a total feed of 2800 m^3 per hour. This is bubbled into the bottom of the cone of the reactor after mixing with 1.5 tons of steam/hr and comes up through about 1 ton of mercury in the base of the cone

The acetylene then bubbles through a mercury-iron sulfate solution maintained at a composition, per liter of solution, of 0.5 gm Hg, 40 gm total iron (of which 4 is ferric), 200 gm $SO_4^=$, and remainder water. This solution also contains 20 cm^3 of NO and has a density of 1.16. The solution fills the tower up to the base of the expanded section and is circulated through an outside pipe back up through the reactor and a portion withdrawn for oxidation of the ferrous iron to ferric with nitric acid.

The bottom of the reactor operates at 97° and the top at 94°. The acetaldehyde, steam and unreacted acetylene separate from the liquid in the expanded section of the reactor at a pressure of 100-200 mm Hg above atmospheric and enter a vertical cooler equipped with V4 A tubes. The gas is cooled to 85° in this cooler and most of the steam condensed and returned to the base of the reactor. The vapors then pass to a cyclone separator to knock out mercury entrainment. This is also returned to the reactor. From the cyclone the vapors pass to a large gas cooler equipped with V_2 A tubes and cooled to 60°. This knocks down a solution of aldehyde in water, and some mercury which is separated and returned to the reactor.

The vapors then pass to a so-called acetic acid tower which is a raschig ring packed tower 1.6 m in diameter and lined with rubber. Solution from the aldehyde washer (see below) is pumped over this tower countercurrent to the vapors to scrub out more aldehyde from the vapors. Last traces of mercury are also knocked down, separated in the cone of the tower and sent back to the reactor. The solution is mixed with the condensate from the gas cooler and delivered as 7% aldehyde solution.

The washed vapor at about 40° is then sent to the aldehyde washer which is a steel disc and doughnut column 1.8 m in diameter. Water from the distillation system containing some acetylene is used as reflux in this column. This column serves to pick up last traces of aldehyde and also to degas the solution of acetylene. Part of the product liquid at 30° is used in the acetic acid washer and part is removed and mixed with the product acetaldehyde. The off gases consisting of recycle acetylene are sent back to mix with fresh acetylene and in a smaller amount are bled off for repurification of acetylene. The total liquid acetaldehyde product is about 38 m^3 per hour per reactor system. It is taken to six coke filters to remove last traces of mercury and is then sent to distillation.

Regeneration of catalyst.

Catalyst solution from the acetaldehyde reactors is continuously being reduced and must be oxidized to maintain constant ferric iron content. A slip stream of about 2.5 m^3 per hour per reactor is withdrawn from the outside liquid recirculation line and sent to a rubber-lined mercury separator and then to one of two degassing towers (rubber lined and filled with raschig rings) in parallel. The base of this tower is heated with direct steam to 100° and the acetylene boiled out of the solution at atmospheric pressure. The vapor from the degasser goes to the primary acetaldehyde condenser, and the degassed solution to the catalyst regeneration system.

In this system the solution is filtered in a rubberized filter press and then is oxidized in two steps tochange the ferrous iron to ferric using HNO_3. The NO liberated is then oxidized with air to NO_2 and converted to HNO_3. The solution oxidizing system consists of six preoxidizers and three afteroxidizers.

The filtered solution is preheated in a V4A preheater and measured into the preoxidizing vessels. In these the solution is treated with 30% HNO_3 at 90° and the solution is then sent to the afteroxidizers where the reaction is completed at 95°. In the afteroxidizers some unreacted solution is added to use up the last traces of HNO_3. The oxidized solution is stored in rubberized tanks and returned to the reactor system.

The oxidizing system is operated slightly under atmospheric pressure using a ventilating system made of V2A. The gases are mixed with air and carried to the NO oxidation and absorption chambers which are three towers in series each 1.6 m in diameter, made of V2 A and filled with raschig rings. The towers are fed separately with HNO_3 solution which is recirculated over a cooler and kept at 30% concentration by addition of water. New HNO_3 is fed in at 60% concentration. The 30% solution is used for solution oxidation and the off gases thrown to the atmosphere.

The filter press cake is treated with caustic soda and lime to neutralize. It is then heated to a red heat in a furnace. The gases produced are cooled in one indirect and two direct coolers and the condensate separated to recover the distilled mercury.

Purification of acetaldehyde.

The 7% acetaldehyde solution is purified by distillation. This is done in four parallel plate columns referred to as acetaldehyde columns. Each column is 2.8 meters in diameter at the base but smaller in the upper section. The solution is heated to 100° by heat exchange with bottoms product and fed to the 16th tray of each tower at a rate of 65 m^3/hr. The column contains 28 plates with 2 meters of raschig rings above the 16th tray and is fed at the base with direct steam. Operation is at 2 atm gage, 135 base temperature and 50° top temperature and the tower is made of V2 A except for the top 8 trays which are steel.

Overhead is taken acetaldehyde which is condensed, cooled and refluxed at 1/3 reflux ratio. The overhead is then sent to a mercury separator and to the top of a degassifier tower. The latter is .8 m in diameter and contains 18 plates. Here the acetaldehyde is stripped of acetylene by operating the tower at 2 atm gage and heating to 50° at the base of the tower with a steam heated heat exchanger. The stripped aldehyde of about 99.9% purity is cooled and sent to storage. The gas goes to the condenser of the acetaldehyde tower, is cooled and separated. It is then sent to a washing tower where the last traces of aldehyde are recovered with a water wash. The gas is then sent to repurification of acetylene. The bottoms from the acetaldehyde tower is about 0.1% acetic acid which is wasted.

A small side stream of 200 l/hr is taken from above the feed plate of the aldehyde column to trap out acetone, diacetyl, crotonaldehyde, water and some acetaldehyde. This is sent to the middle of a raschig ring filled tower made of V2 A operated at atmospheric pressure and heated with direct steam. The overhead vapors are removed at 30° after passing through a water cooled partial condenser for providing reflux and are handled through the washing tower mentioned above to scrub out acetaldehyde. The bottoms from the column are sent to an acetone purification system to recover acetone.

The first tower in this system (called an acetone fore-column) is a 0.5 m diameter packed tower operated at atmospheric pressure, 42° top temperature, 85° base temperature and 4:1 reflux ratio and equipped with an external steam heated reboiler. From the top of this tower is taken acetone and acetaldehyde and from the bottom diacetyl and crotonaldehyde which are sent to the sewer.

The overhead from the first acetone tower is sent to a second packed tower 0.5 mm in diameter operated with a partial condenser for reflux and with an overhead condenser for product. Direct steam is used. Overhead acetaldehyde is removed at 35°, condensed and sent to the water wash tower of the aldehyde system. The bottoms are removed at 65° and sent to a pure acetone tower. This column is of the same size as the other two acetone columns and is equipped with a partial condenser for reflux and an overhead product condenser. Reflux is also added with the feed to the column. Pure acetone is removed overhead at 55°, condensed and sent to storage. The water at the base of the column is discarded at 75°. This column uses an externally heated reboiler. Acetone production is about 24 kg/hr from the entire system.

Acetylene repurification.

In order to prevent building up of impurities in the recycle acetylene used for aldehyde synthesis, a slip stream from the recycled gas having a purity of 70-75% is repurified by absorption to about 96%. The recycle gas is compressed to 4 atm gage, separated from liquid, and sent first to a 1.0 m diameter steel packed tower called a forewasher. In this tower, traces of aldehyde are removed from the gas by water scrubbing. The gas then goes to a main washer 2.4 m in diameter and constructed with perforated plates where it is washed with 0.5% sodium hydroxide to remove CO_2 and to absorb the acetylene. The solution is then sent to a tower at a lowered pressure to release the acetylene from the caustic solution. The released gas is acetylene of 96% purity. The undissolved gas from the caustic washer containing 25% acetylene is compressed to 7 atm gage, separated from liquid and scrubbed with a large amount of water in an afterwasher similar to the first washer. The acetylene-water solution is returned to the aldehyde washer in the aldehyde reactor system. The off gas, containing 3% acetylene, is discarded to fuel.

ALDOL PRODUCTION AND PURIFICATION.

Summary.

Aldol is made by treatment of acetaldehyde with dilute KOH at 20° - 30° in a long heat exchanger cooled with water. The conversion is 46-47% per pass and the ultimate yield 88% of theory. The aldol is treated with diluted phosphoric acid to precipitate potassium phosphate which is separated. The crude aldol is then separated from unconverted acetaldehyde by distillation. The total capacity of the system using 4 reactors is about 10,000 T/mo. There are six reactors available, one of which is now partly dismantled. Two sets of three available distillation units will handle this quantity.

Aldol production.

Pure acetaldehyde is mixed with about an equal
part of recycle aldehyde and pumped through the insides
of the tubes in a reactor made up as a long horizontal
tubular heat exchanger, cooled on the outside of the
tubes with water for about 1/3 of the surface. Each re-
actor has a volume inside the tubes of 10-26 m^3 and the
various sections are stacked one above the other. The re-
actor tubes are of iron and about 20 mm in diameter. Each
reactor is made up of 12 horizontal runs 6 meters long
each, divided into two sections horizontally and six ver-
tically. There are about 100 tubes in a bundle which is
held between two fixed tube sheets. Each reactor has 720-
960 m^3 of cooling surface.

The temperature in the reactor is maintained at 20°- 30° . From 0.02-.1% KOH based on aldehyde is injected into the aldehyde just before the circulating pump as a 1.4 - 11.2% solution depending on the water content of the circulating stream.

The aldehyde-aldol mixture is held at 46-47% conversion, by controlling KOH concentration, withdrawal rate etc. Rapid recirculation through the heat exchangers is required, amounting to approximately 20 times the fresh input of aldehyde or 180-250 m^3/hr. The average time of contact is 2-3 hrs.

A typical analysis of the crude aldol shows 52.84% acetaldehyde, 0.32% crotonaldehyde, 44.80% aldol and residue, and 2.04% H_2 O. This product is withdrawn from the circulating system and sent to a mixing vessel holding 300 l. In this an 8.6-17.2% solution of phosphoric acid is added and the liquid allowed to stand for one hour in a vessel to permit the potassium phosphate to form large enough crystals for centrifuging. The solution is centrifuged to remove phosphate, then sent to a leaf filter and finally to a mixer, before being purified by distillation.

The whole operation is conducted with controlled conversion of 46% to keep from production of too much crotonaldehyde, higher aldehydes, etc. The caustic addition is made so that the phosphate crystals come out at pH 8.0-8.5, which is controlled by Bromeresol purple indicator. This yields finally an aldol of pH 6.1. The heat problem in the reactor is not too large (300 K cal/kg acetaldehyde reacted) so the cooling water is only used in part of the reactor system. However, if the temperature exceeds 25° the by-products rapidly increase so that instead of using 114 kg aldehyds/100 kg aldol, the requirement rises to 120 kg. Another difficulty is the fact that aldehyde has a density of 0.8 whereas aldol is 1.0 so that there is a shrinkage in volume as the reaction proceeds. Care must therefore be taken to keep the reactor full of liquid at all times.

Purification of Aldol.

The crude aldol is pumped through a filter to three pure aldol distillation towers in parallel. Each tower contains 23 plates and the feed is on the 8th plate. Here at atmospheric pressure aldehyde is taken overhead at 21°-25° and at a reflux ratio of 1/5. The bottoms from the tower is sent to a series of three heat exchangers, heated with 3.0 atm (gage) steam to heat the aldol from 70° - 80° to 100°-110° and flash off surplus water, which returns to the base of the tower. The aldol is then quenched to 65° with an equal amount of finished cold aldol (to prevent side reactions) and cooled in trickle cooling coils to 30° - 35°. It then goes to a mixer and storage. The pure aldol has a pH of 5.7, with a typical analysis as follows:-

Aldol	72.82%
Acetaldehyde	4.65%
Crotonaldehyde	1.59%
Residue	2.60%
Water	18.34%

Overall yields in the middle of 1944, based on 46% conversion per pass were per 100 parts of aldehyde by weight:-

Aldol	88.0 parts
Acetaldehyde	5.61 "
Crotonaldehyde	2.42 "
Residue	3.14 "
Loss	0.83 "

BUTYLENE GLYCOL PRODUCTION AND PURIFICATION.

Summary.

1,3- Butylene glycol is produced by the hydrogenation of aldol in continuous vertical reactors at 300 atm and 50°- 150° over a catalyst made of 17-20% Cu, 0.7 - 1.0% Cr on calcined silicagel. There are four reactors operating at the above conditions, one unit at 700 atm. and one smaller unit is used for crude butanol hydrogenation. The latter operation serves to hydrogenate impurities in butanol and permit their separation. Each of the five reactors will produce 16.0 T of butylene glycol per month. The butol is purified by distillation in two trains.

Butylene glycol production.

So called "pure aldol" containing about 72% aldol is hydrogenated in five vertical continuous reactors. These reactors are 18 m. high, 0.8 m. in diameter and have a volume of 9 m^3 each. The vessels are constructed for high pressure (300 or 700 atm) of Cr. - Mo. steel and are copper lined on the inside. They are filled with 8 m^3 of B.B.E catalyst made of 1-4 mm grains produced by impregnating dried and heated silicagel with the nitrates of copper and chromium so as to have 17-20% Cu and 0.7-1.0% Cr. on the finished catalyst. The impregnated granules are dried and heated to 450° C.

In starting up operations the reactor is pressured with 100 atm of N_2. About 7000 m^3/hr of gas is recirculated over the catalyst and the reactor gradually heated from 60° to 200°. H_2 is then introduced so as to have the reactor at 300 atm and circulating gas at 80% H_2 and 20% N_2. This is circulated for about

48 hours until the catalyst is reduced to the active metals. The temperature is then reduced to about 50°.

The aldol is heated in three parallel preheating coils to 50°-70° and enters the top of the reactor at a rate of 4.1 m^3/hr per reactor. H_2 is also passed in at 50°-70° and 300-700 atm and at a rate of 13000 m^3/hr per reactor to remove reaction heat. Of this amount 1100 m^3 is fresh hydrogen and remainder recycle. The net H_2 usage is therefore 1100 m^3/hr. Both reactants pass down over the catalyst bed. The reactor is equipped with cone baffles about every two feet for liquor redistribution. The hydrogen is preheated by sending part through a steam preheater and mixing with cool H_2. The mixed gas is then partly sent through a heat exchanger against hot reactor products and mixed again to give the desired final temperature.

The reaction releases considerable heat and raises the temperature 50°- 90° depending on the catalyst age. The outlet temperature at the base of the reactor is therefore 90°-160°. When the catalyst is new the inlet is 50° and the outlet 90° and when spent the inlet is 70° and the outlet 160°. As the catalyst ages the side reactions increase, particularly to butanol, and when this becomes excessive the catalyst is dumped and copper recovered or it is transferred to butanol hydrogenation. On the average the catalyst life is 2-3 months and there is a conversion of 193,000 kg pure aldol to butol per 100 kg catalyst. The reaction is carried to completion in one pass (to 0.1% aldehyde content) at a yield of 93% of theory.

The reaction product passes through heat exchange with incoming H_2 where it is cooled to 50°-120°. It then passes through a cooler where it is further cooled and sent to a liquid separator, a slightly inclined horizontal vessel. The gas is separated and recycled with 1100 m^3/hr of fresh H_2 97.8% pure, and the liquid products sent to several separators operated at atmospheric pressure.

The "pure" aldol feed and the crude butol product have the following typical analyses:-

Pure aldol		Crude butol.	
Aldol	71.83%	Butol	67.48%
Acetaldehyde	4.98%	Ethylalcohol	5.31%
Crotonaldehyde	2.13%	Butenol	5.10%
Residue	3.11%	Residue	3.10%
Water	17.95%	Water	19.01%
	100.00%		100.00%

The H_2 used contains about 2.2% of inert gases, as noted above, most of which is N_2. It is therefore necessary to bleed off 100-200 m^3 per hr of recycle H_2 to keep the concentration of the recirculating stream at around 80% H_2 content.

The 700 atm. reactor will handle about 50% more production than a 300 atm. unit, but no conclusions are yet available regarding the best operating pressure. Some work has been done on nickel bearing catalysts, but this requires H_2 of .001% CO or less for good operation. Raney nickel was also studied but such an active catalyst is not required.

Crude butanol, produced as a byproduct of the butol distillation is hydrogenated in the small (0.8 m. dia) hydrogenation reactor at 300 atm and 200-210° using spent butol catalyst. The feed contains 0.4% butyraldehyde, 4-10% butolacetal, 0.1% esters and 1-3% crotylalcohol as impurities. The butyraldehyde and crotylalcohol are hydrogenated to n-butanol and the butolacetal to secondary butanol and 1,3 butylene glycol. The esters are saponified.

Purification of Butylene glycol.

Crude butylene glycol is purified in two trains of four distillation columns each. In addition there is a single tower for the recovery of crude ethanol and crude butanol, and a set of towers for the recovery of pure butanol.

The crude butylene glycol is fed to the 12th plate of the first column at a rate of 18 tons/hr. This tower is 1.6 m in diameter and in one train is 32 m high and contains 30 plates and in the other is 27 m high and contains 45 plates. Here at 0.7 reflux ratio, 85° top temperature, 117° base temperature and atmospheric pressure water, alcohol and butanol are removed overhead and the butol, most of the water and residue are withdrawn from the base.

The crude butol from the first column then enters the 12th plate of the second tower which operates at 51 mm pressure, 98° overhead temperature and 157° base temperature. This column is 2.6 m in diameter, 22.5 m high and contains 30 plates in the first train and is 2.6 m in diameter, 26 m high and contains 30 plates in the second train. At a reflux ratio of 0.2 water is removed from the top of the column and concentrated butol from the base.

The butol is then fed to 12th plate of the third column which operates at 29 mm pressure, 120° top temperature and 174° base temperature. This column is 3.0 m in diameter 22.5 m high and contains 30 plates. Overhead is taken 12 tons per hour of pure butylene glycol of 98.5 - 99.5% purity and residue is withdrawn from the base. The reflux ratio is maintained at 0.4.

The residue from the third column contains 30% butol which is recovered in the fourth column. This is a raschig ring packed tower 0.6 m in diameter and 12.6 m. high. The feed enters the middle of the column which operates at 4 mm pressure, 85° top temperature, 165° base temperature and a reflux ratio of 0.4. From the top is taken recycle butol which is sent to a point below the feed plate of the second column in the train. From the base of the fourth column is taken butanol residue.

The purified butol contains approximately the following impurities:-

Aldehyde	...	0.05%
Acetal	...	0.10%
Esters	...	0.14%
Unsaturates	...	0.13%
Water	...	0.39%

The crude ethanol-butanol-water mixture obtained overhead in the first column of the butol purification train is sent to the 12th plate of a tower 2.6 m in diameter, 27 m high and containing 60 plates. This column operates at atmospheric pressure, 78° overhead temperature, 95° base temperature and 5 reflux ratio. Overhead is produced crude ethanol and from the base is taken crude butanol. The crude butanol is hydrogenated in the small reactor of the hydrogenation system and is then further purified. The compositions of the various streams are about as follows:-

Crude ethanol	
Aldehyde	0.42%
Acetal	0.14%
Esters	0.02%
Unsaturates	0.10%
Ethanol	94.90%
Water	4.42%
	100.00%

	Crude butanol	Hydrogenated Crude butanol
Butyraldehyde	0.4	0.0
Acetal	4.10	0.14
Esters	0.1	0.01
Crotylalcohol	1-3	0.05
Ethanol	2-3	2-3
Hexanol	3-5	3-5
Sec.Butanol	-	1.5-6
1,3 Butol	-	2.5-4
Water	18-21	18.0-21
n-Butanol	57.5-71.5	60.8-72.8
	100.0	100.0

The hydrogenated crude butanol is purified in three continuous and two batch stills. The first column takes ethanol, acetal and secondary butenol overhead. The second, fed with the bottoms from column one takes off a constant boiling mixture of 53% butanol and 47% water which separates into a butanol-rich and a water-rich layer. The butanol-rich layer is used for reflux. The bottoms from the second column are fed to the third column where pure butanol is removed overhead and residue withdrawn from the base. The overhead from the first column, the water-rich layer and the residue are worked up in two batch columns to produce hexane, ethanol, sec-butanol, ethylbutanol (hexanol) and 1,3 butol. The data on the various columns are as follows:-

	Column I	Column II	Column III	Batch Column I.	Batch Column II
Diameter	1.0 m	1.0 m	1.0 m	2.5 m	2.6 m
Height	26.9 m	26.9 m	21.9 m	27.6 m	27.6 m
Plates	45	30	30	45	45
Reflux ratio	15-20	-	-	3.0	-
Top Temp.	85°	94°	121°	-	-
Bot.Temp.	92°	98°	145°	-	-
Pressure	1 atm	1 atm	1 atm	1 atm	1 atm

An approximate material balance on the butol distillation plant is as follows:-

Input-Crude	butol feed	146 parts
Output Pure	butol	100 parts
	Ethanol	7.3
	Butanol	5.6
	Butolresidue	3.8
	Hexanol	0.4
	Sec-butanol	0.2

~~BUTADIENE PRODUCTION AND PURIFICATION.~~

Summary.

Butadiene is made by the dehydration of 1,3 butylene glycol in the presence of steam over sodium phosphate on coke catalyst at 280° and 1 atm. The plant contains 18 reactors of somewhat varying sizes each having a capacity of 160-190 tons butadiene per month. The butadiene is purified by distillation. The conversion per pass is 100% and the ultimate yield 81% of theory.

Butadiene Production.

500-700 kg/hr of 1,3 butylene glycol per reactor is preheated with hot water at 45 atm pressure to 210° and then mixed with an equal quantity of steam at 400° and 1 atm gage. The mixture then flows upward through ~~a dehydration reactor which is maintained at 280 and~~ 1 atm pressure by means of 65 atm. hot water where reaction proceeds to completion to the formation of butadiene. The yield (counting distillation loss) is about 81% of theory with most of the side reactions to partially dehydrated butol products.

The reactor is a vertical cast iron cylinder 3 m in diameter by 5 m high made in segments and containing 12 m^3 of catalyst (12 tons). The cylinder is made up of a series of circular segments stacked one above the other and bolted together with flanges and asbestos gaskets. Each segment is about 1 ft high and between each segment is a pancake coil made of steel and through which high pressure hot water is circulated to maintain reaction temperature. The center 1 ft diameter of the reactor is filled with graphite plugs to prevent bypassing. The outside of the reactors are insulated with segmental removable insulation. Proper spacing between the tubes in the pancake coil is allowed to permit catalyst to be fed down from the reactor top.

The catalyst is 5-8 mm coke granules treated with sodium phosphate, phosphoric acid and butylamine phosphate solution to make a catalyst finally containing 35-38 % sodium phosphate, 3.5-3.8% H_3PO_4. This is made by impregnating the coke so that it contains per 100 parts of coke 56 parts Na_2HPO_4, 8.5 parts free H_3PO_4 and sufficient butylamine to neutralize the free acid. The butylamine seems to make the phosphate active after drying of the catalyst. The coke after treating with the solution is heated to convert the phosphate partly to

$(Na\,PO_3)_2$ and partly to $Na_2\,P_2O_7$ but not as far to the latter as is used at Ludwigshafen for 1,4 butylene glycol dehydration. The catalyst gradually hardens, clinkers and carbonizes so that in 25-28 days the pressure drop has increased so much and the catalyst activity has decreased so much that the catalyst is changed. This can be done in 24 hrs by pulling off the reactor top, then removing each segment of the reactor and forcing out the catalyst between the pancake coils. The catalyst is leached to remove phosphate and the phosphate evaporated and reused. The coke is discarded. Earlier, graphite was used as a carrier but only coke is now used. Graphite and coke seem to give identical performance.

From the top of the reactor the product gas (which is practically free of butol) is sent to a cooler to separate H_2 0 and oil. The average composition of the C_3 and heavier products is 80% butadiene, 2% propylene, 2% butyraldehyde, 10% allylcarbinol, 1% 2-ethylhexanol, 4% heavier oils and 1% butenes.

The reactor gas leaves the cooler at 25 and goes to a compressor where it is compressed to about 200 mm above atmospheric and is fed to the base of a 1.3 m diameter, 10 m high column containing 25 plates. The oil leaving the cooler is separated from water and both later purified. The reactor gas is scrubbed with 20° water in the column and the water joins the water stream leaving the separator after the primary cooler.

The scrubbed gases then go to a gasholder and are then compressed to 4.2 atm gage, and cooled to 25° in a heat exchanger. Gas is separated from the liquid and cooled to - 25° to knock back condensibles and is then vented to the atmosphere. The liquid from the exchanger is separated from water, and then sent to a purification train to purify the butadiene. On the way methanol is added to separate last traces of water, which is removed from the hydrocarbon stream.

The crude butadiene is fed first to a propylene tower which is 1.0 m in diameter, 10 m high and which contains 30 plates. This column operates at 1 atm; - 46° top temperature, 0° base temperature and at 7 reflux ratio to take overhead pure propylene and to remove below propylene-free crude butadiene. The propylene is compressed to 6.1 atm gage, used for reboiling heating medium in the column reboiler and then sent to storage. Part of the propylene is returned to the column top as reflux after going through a heat exchanger.

The depropanized butadiene is sent finally to a pure butadiene column to remove about 1% heavier materials. This tower is 1.6 m in diameter, 10 m high and contains 30 plates. It operates at 1 atm., - 1° overhead temperature, 35° base temperature and at 0.2 reflux ratio. Butadiene of 99.5% purity is taken overhead and butadiene residue withdrawn from the base. This is mixed with other oils from the process for further recovery of useful by-products. No indication of butadiene polymer formation has been found in these towers except for a little popcorn polymer in dead spots.

The oil separated from the primary cooler is sent to a packed column operated at 3 atm gage, 150° base temperature and 50° top temperature to remove gases from the oil. The gases are returned to the suction of the blower feeding the water-wash column. The water streams from the separator and water-wash columns, containing 5% oil in solution, are fed to a 1.2 m diameter tower packed with raschig rings. Steam is blown into the base of this column and overhead at 93° is taken oil which is sent to the first packed column used as a oil degassifier.

All of the oil from the first column is fed to a batch tower together with residue from the pure butadiene still. This tower is 1.2 m. in diameter and contains 45 plates. The oil is batch distilled at atmospheric pressure to produce crude butyraldehyde, a 80-110° fraction and a crude allylcarbinol. The residue is further batch distilled at 5 mm pressure to produce two overhead fractions and residue referred to as hexantriol is used in the manufacture of a lacquer substitute. The allylcarbinol is recycled to the reactor feed.

<u>Butadiene analysis.</u>

Typical and specification butadiene produced at Huls is as follows:-

	Percent by weight.	
	Typical.	Specification
Butadiene	98.5-99.5%	98.0% min.
Active oxygen	0.0005.0.001%	0.001% max
Acetaldehyde	0.002-0.004%	0.005% max
Water	0.01 - 0.03%	0.05% max
Nesslers reagent	Colorless to yellow.	yellow
	Clear to faint turbidity.	slight turbidity
Jlosvay reagent	Colorless, clear	faint rose color
Turbidity in methanol	—	No turbidity

(a) initial E= 0.00-0.04
(b) after 20 hrs E=0.7-0.9

I. Butadiene determination.

Butadiene is determined either by the volumetric maleic anhydride method or gravimetrically. The gravimetric bromination method is as follows:

Butadiene gas (50-250 mg or 20-100 cc) is condensed in an evacuated, weighed weighing tube. This is sealed, reweighed and put into a 250 cc bromination flask which is stoppered with a ground joint and a color attachment. This is weighed and evacuated. Through the color funnel 1 cc of bromine and 5 cc of chloroform is added without allowing air to enter and the seal broken. The flask is slightly agitated and rotated and allowed to stand 5-6 hrs or overnight. After this time most of the excess bromine and chloroform is distilled off carefully at a slight vacuum. The remainder is removed under high vacuum, heating slowly with warm water at 40°. The flask is then allowed to stand 1/2 hr at room temperature under high vacuum. If the solution is not clear and colorless the material is dissolved in 10 cc of chloroform and evaporated at body temperature. In this way the colored impurities are largely removed and at the same time the butadiene-tetrabromide is not volatilized by these mild conditions. The test is continued under high vacuum until the weight is constant. The flask is weighed and the butadiene content calculated allowing for blank errors.

The blank errors of the method are about 2 mg or 0.1 cc butadiene. In order to minimize this both stopper and stopcock grease must not be made of fats.

To hold vacuum phosphoric acid is used as a stopcock grease. It is also necessary to make sure the vacuum is not too suddenly released or there will be losses due to spitting and atomization. If e is the original weight and a the final weight and b the blind error the % butadiene is calculated as:

$$\% \text{ butadiene by weight} = \frac{(a-b)\,54.05 \times 100}{373.7 \times e}$$

II Acetaldehyde and active oxygen determinations.

Details of these methods were obtained but it does not appear necessary to reproduce these in this report.

BENZENE PURIFICATION AND DISTILLATION.

Summary.

Benzene is obtained as a crude product from various coal tar plants in the Ruhr area and is purified at Hüls to make it suitable for conversion to ethylbenzene and styrene. It is first washed with H_2SO_4, NaOH and water and then distilled to remove CS_2, aliphatics and other aromatics such as toluene.

Benzene Purification.

The crude benzol is taken from storage and first treated in two countercurrent continuous washers with sulfuric acid. This system consists of two separating vessels and two mixing systems, the latter made up of a series of fifteen obstructions similar to a trombone cooler or a disc and doughnut mixer. In the first-mixer 3% of 80% H_2SO_4 is contacted with benzene at a temperature of 25° - 28° and a pressure of 2.5 - 3.0 atm, gage. The separated liquid benzene is removed and sent to the next mixer and separator at 1.5 atm gage where it is mixed with 3% of 96% H_2SO_4. Some of the spent acid from this separator is sent to the first one to maintain acid strength. The rest is recirculated through the mixers and then discarded to the sewer.

The next step is a similar treatment in two mixers and one separator with five percent of 4% NaOH solution at 0.8 atm gage. The last step is washing with 5% of calcium free water, which is then separated from hydrocarbon traces in a sewer separator. The washed benzene is refined further by distillation. Each of the above mixers has a volume of about 0.8 m^3 and the separators 4.5 m^3. The normal throughput to the system is 3,500 kg/hr of crude benzene and there is a circulation of 3000 kg/hr of sulfuric acid in each mixer and 2000 kg/hr of NaOH solution. The crude and washed benzene have the following analyses:-

	Crude benzene.	Washed benzene.
Initial B.P	79°-80°	79-80°
95% off at min	85°	85°
Density at 15° min.	0.882	0.883
H_2SO_4 No.max	10	0.5
Bromine " "	1.5	0.3
Melting point	4.0°-4.5°	4.0°-4.5°

Benzene Distillation.

The benzol is refined to pure benzol in three trains of two columns each in series. Two systems have a capacity of 2000 T/mo and the third of 4000 T. It is preheated first by heat exchange against benzene condensate from the second tower and flows to the 9th-14th plate of a 30 plate tower. This tower is made in two sections, the top one of 15 plates being 0.6 min diameter and the bottom section of 15 plates 0.8 m in diameter. The plates are spaced 250 mm apart. This tower operates at atmospheric pressure, 45° top temperature and 83° bottom temperature at a reflux ratio of 50. About 2920 kg/hr is fed to a tower and overhead is taken 29 kg/hr consisting of 30-40% CS_2, aliphatics and some benzol. The condenser at the column top is operated as a dephegmator.

The benzol from the base of the first column is fed to the 15th-25th tray of a second tower 1.0 m in diameter and containing 65 plates. This tower operates at 1 atm pressure, .79° top temperature, 120° bottom temperature and a reflux ratio of 1.0. Overhead is taken 2770 kg/hr of pure benzene and below 702 kg/hr of crude toluene.

One set of benzene towers is used intermittently to separate benzene, toluene and residue continuously from the crude toluol which contains 10% benzene and 10%-20% heavier than toluene. The residue is used for solvents. The two smaller benzene trains are in condition to operate but the larger one has been slightly damaged.

The analyses of the pure benzene is as follows:-

Boiling range	0.2° - 0.4°
H_2SO_4 - No.	0.15 avg 0.30 max.
Bromine- No.	0.15 avg 0.30 max.
Melting point	+ 5.3°
Density at 15°C	0.883

ETHYLBENZENE PRODUCTION AND PURIFICATION.

Summary.

Ethylbenzene is made by the continuous alkylation of benzene and ethylene in vertical, jacketed enamel-lined reactors with $AlCl_3$ catalyst. Dealkylation of polyethylbenzenes also takes place at the same time. The $AlCl_3$ usage is about 2.5 Kg/100 Kg ethylbenzene. The reactor product contains 45% benzene, 38% ethylbenzene and 17% polyethyls, which is separated in a distillation train and the benzene and polyethyls returned for further reaction. The system consists of 8 reactors each having a capacity of 800 T/month ethylbenzene, but total production is limited to 2000-3000 T/month by distillation capacity.

Ethylbenzene production.

The ethylbenzene plant consists of 8 reactors 1.4 m in diameter and 12 m high which are enamel-lined (Pfaudler). These reactors are split into four separately cast steel sections, bolted together with flanges using asbestos-rubber gaskets, and each having a separate cooling jacket. The reactors are also equipped with a dome and a bottom with suitable entrances at the bottom for ethylene, ethylbenzene, polyethyls and recycle catalyst complex. The top is provided with an 8" pipe for the injection of $AlCl_3$, a vapor line leading to a condenser and a return line for condensate. There are two enamelled water cooling coils in the vapor space of the reactor.

Ethylene at 200 mm water pressure is taken from a gasometer and compressed to 2 atm. in an Elmo pump (similar to a Nash Hytor) using polyethyls as liquid medium. It is injected near the base of the reactor through a pipe pointing downward toward the benzene inlet. Benzol and polyethyls are introduced at the center of the base of the reactor. Complex is introduced also near the bottom. The mixture of ethylene, benzol, polyethyls and complex flows upward to a level in the reactor 10 m from the base thus having a total liquid space of 13.8 m^3. It then overflows to a jacketed, cooled separator, where the alkylated liquid is decanted off and the complex returned by gravity to the base of the reactor. The separator has a volume of 3 m^3 and operated at 80°.

The reactor is maintained at 100° bottom temperature and 90° top temperature by cooling in the jackets. The pressure is about atmospheric. At the start it is necessary to heat the base of the reactor since the reaction does not proceed by itself until the temperature is in the range of 90°. The reaction is exothermic (27 K cal/gm mol) and hence cooling in the jackets is required after the reaction starts.

The vapors leaving the top of the reactor (consisting largely of benzene) are condensed by a total condenser and refluxed back to the column top. The off gases containing largely ethane, inerts and traces of unreacted ethylene are rejected from the condenser after scrubbing out HCl with water and passing through an H_2SO_4 seal to prevent moisture leaking back to the reactor system.

The Al Cl_3 is added to the reactor top by means of an 8" dia pipe which extends below the liquid level. This has a quick-opening seal at the top into which Al Cl_3 is added by means of a small hand scoop several times an hour at a predetermined rate.

The benzene and recycle polyethyls are dried over solid caustic soda prior to introduction into the reactor. The ethylene comes from various sources and is water free and about 95% pure. It contains largely methane, ethane and about 1% acetylene as impurities.

The liquid product from the separating cooler is treated with soft water in an acid-brick lined washer, separated and then washed with 20% NaOH and again separated. It then goes through a water wash to a receiving tank and a solid caustic drier before being sent to distillation. The drier is cone shaped at the base to remove liquid caustic, and fitted with a top to permit addition of solid caustic.

About 50-55% of the benzol is alkylated per pass and the average throughput per reactor is as follows:

300 m^3/hr ethylene
450 Kg/hr polyethyls
2000 Kg/hr benzol
35 Kg/hr $AlCl_3$

As noted above this gives about 800 T/mo of ethylbenzene per reactor. The reactor product has the following composition:

45% benzene
30% ethylbenzene.
11% diethylbenzene
5% higher alkylated benzenes (through hexa-ethyl)
1% residue (used for plasticator)

Earlier in the development a continuous screw conveyor was used to inject $AlCl_3$ but this was later abandoned at Huls. Acid brick linings and Raschig rings were also used in the reactors to ensure distribution, but this was found unnecessary, and in fact harmful to the enamel. Currently all lines in contact with reactor product are coated with a phenol formaldehyde resin called phenytal which is made at Huls. Plug cocks are used throughout the system. Considerable trouble has been found in maintaining tight seals between the reactor sections (due to warping of the flanges). It is now expected that reactors will last 1-2 years before the enamel gives trouble although the Germans have not been able to obtain new enamelled sections in recent months and have had to resort to acid brick linings. Troubles with pinholes, etc. in the enamel have not been important.

The overall yield on benzene has averaged 94% of theory and on ethylene 93% of theory including distillation losses. The overall $AlCl_3$ usage is about 2.5 Kg/100 Kg net ethylbenzene and this is stated to be added roughly as follows:-

I (Alkylation)	II (Dealkylation)
600 liters benzene	200 liters benzene
100 m^3 ethylene	100 liters polyethyls
5-7 Kg $AlCl_3$	3 Kg $AlCl_3$

From time to time fairly large quantities of diethylbenzene have been removed and used as an ingredient of aviation gasoline under the name of Kybol.

Ethylbenzene purification.

Crude ethylbenzene, after washing, is first partially purified by distillation at atmospheric pressure in one of three two column trains. Of the three, two have a capacity of 2000 T ethylbenzene per month each and the other 4000 T/mo. The two smaller units are generally used.

About 7385 Kg/hr are fed to the 13th to 19th plate of the first tower which is 1.6 m in diameter, 16 m high and contains 45 plates, with 350 mm spacing between plates. A reflux ratio of 2.5 is used. Pure benzene containing not over 0.25% ethylbenzene and having a boiling point range of 5-8° is taken overhead at 80°C and returned for alkylation. This quantity is 3320 Kg/hr.

From the base of the first tower at 156° the residue is sent to the second column which is 1.1 m diameter, 16 m high and which contains 57 plates spaced 300 mm apart. This tower operates at 1.0 reflux ratio, atmospheric pressure, 136° top temperature and 196° bottom temperature. Overhead from this tower is taken 2780 Kg/hr of pure ethylbenzol (0.3°C boiling range, H_2SO_4 number 0.15, Bromine number 0.10-0.15). Feed to the second tower is sent to the 5th-21st plate (normally the 17th).

The residue from the second column in the first distillation train is sent to a set of three two-column trains operated at a top pressure of 10 mm. The feed enters the 15th tray of the first column which is 1.4 m diameter, 16 ft high and which contains 38 plates. The top pressure is 10 mm, the bottom 70 mm and the reflux ratio is 1.5. From the top of this column at 60° is taken 840 Kg/hr of diethylbenzene having a boiling range of 170-185° (usually 173-180°) and polyethyls and residue are removed from the base of the column at 145°.

The last column is 0.8 m. in diameter and 8 m high, and is filled with 1" Raschig rings. It operates at 10 mm top pressure, 110° top temperature, and 180° bottom temperature and without reflux. Overhead is taken 260 Kg/hr of higher alkylated benzene which are sent back for dealkylation and the residue from all trains is withdrawn to a single 1m^3 flash pot. This pot is heated to 200° with a steam jacket and overhead is taken 50 Kg/hr of higher alkylated products. The residue of about 100 Kg/hr and having a gravity of 1.0 is removed and used as plasticator or for diluting styrene bottoms. The pot operates at 10 mm pressure and about 120 vapor temperature.

All towers are equipped with outside vertical thermo-syphon reboilers. Vacuum is produced by direct mixing of vapors with water or by cooling the vapors by means of a heat exchanger. In either case a steam jet and a barometric leg is used. Benzene, diethylbenzene and the two streams of polyethyls are recycled to the alkylators for conversion to ethylbenzene.

STYRENE PRODUCTION AND PURIFICATION.

Summary.

Styrene is made at Huls, as at all other German synthetic rubber plants, by the catalytic dehydrogenation of ethylbenzene in tubular reactors heated with flue gas. The best monthly production to date has been 1800 T/mo. The process operates at about 600° C and 1 atmosphere pressure and with 1.25: 1.0 to 1.5: 1.0 steam to hydrocarbon feed ratio by weight. The tubes are made of V_2A metal (18 Cr.- 8 Ni) lined with 1 mm of copper manganese (98% Cu. 2% Mn.) to prevent thermal cracking effects. The catalyst is extruded and is made of 85% ZnO, 3% Al_2O_3, 5% CaO, 2% K_2SO_4, 3% K_2CrO_4 and 2% KOH. The conversion per pass is about 40%, the ultimate yield 90% or better, including distillation losses. No regeneration of catalyst is required and the catalyst life is about nine months. Purification is carried out by fractional distillation under vacuum.

Styrene Production

The Huls plant contains 18 reactor systems of which twelve are in one building and six in another. In addition two more reactors are partly completed and there is space for four more. Each reactor system consists of a vaporizer, two heat exchangers, a reactor, a precooler, a condenser and a separator. One reactor system was damaged.

Ethylbenzene and recycle ethylbenzene and steam are mixed in the ratio of 1.25: 1.0 to 1.50: 1.0 steam to ethylbenzene by weight. About 450 kg. of ethylbenzene per hour is used per reactor per hour which is sufficient to produce 100 - 120 T. styrene per month. The hydrocarbon-steam mixture passes through a vaporizer and two heat exchangers before entering the reactor at about 595°. The vaporizer raises the temperature from 20° to 175°, the first heat exchanger from 175° to 400° and the second heat exchanger from 400° to 575°. Heating is accomplished by passing hot flue gases from the reactors through the second heat exchanger, hot reactor gases through the first heat exchanger and flue gas from the second heat exchanger through the vaporizer. The reactor product gases are cooled from 590° to 330° before going to the precooler and condenser.

The preheated feed enters the top of the reactor and flows down through a number of 4" - 8" tubes, 2 meters long, in which catalyst is placed. The tubes are heated on the outside by flue gas produced by burning coal gas. The flue gases leaving the reactor then pass in heat exchange as indicated above and return to the combustion space for recirculation, a portion being rejected to the atmosphere to make up for new flue gas production.

The reactors are made in several sizes, all of which contain about 2 m^3 of catalyst. The average diameter is 2.2 m. Each reactor is a vertical metal cylinder lined with brick and with a dome and bottom. The shell is divided by a central metal vertical baffle and a number of horizontal baffles are also used to improve heat transfer. Tubes 4" - 8" diameter and 2 meters long made of V_2A and lined with a 1 mm. Cu-Mn liner (98% Cu, 2% Mn) are placed vertically between upper and lower tube sheets. The dome, bottom and tube sheets are all lined with 1 mm of Cu-Mn and weep holes are extended out through the flanges at the dome and base to prevent buckling of the liner. The liner is inserted loosely. Each reactor has 22, 26 or 92 tubes depending on the tube size. The outside of the reactor is insulated.

The flue gas for maintaining temperature in the reactor tubes is produced in two combustion chambers on opposite sides of the reactor (one for each side of the reactor). Each chamber has three burners which use coal gas as fuel. In one type of reactor air is blown in under pressure, using one blower for each three reactors. In the other type the circulation is at about atmospheric pressure and no high pressure air blowers are required. The flue gas is circulated around the tubes in the reactor near the top and then withdrawn near the base of the reactor, used as indicated above for heat exchange and recycled with a blower. The flue gas enters at 700°, leaves at about 640°, drops to 525° in the heat exchanger, and then to 380° in the vaporizer. It is then drawn to the recycle flue gas blower where it is sent back to the combustion chamber at 360°.

The catalyst used in this process contains 85% ZnO, 3% Al_2O_3, 5% CaO, 2% K_2SO_4, 3% K_2CrO_4 and 2% KOH. It is made by mixing the three oxides and wetting the mix with solutions of the potassium salts. The product is extruded, dried and calcined at 450°. The ZnO must be of good quality and all reagents must be free from chlorides. The catalyst originally was made without potassium or chrome, but the yield was poor (75% versus 90 - 96% with present catalyst). Tests have been made at various steam: hydrocarbon ratios and operation below 1.25 ratio results in coke accumulation. Higher ratios help ultimate yield by a very small amount. Conversion per pass is maintained at 38-40% by control of reactor temperatures and this range appears optimum. Under these conditions no regeneration is required and catalyst life is about nine months. The catalyst was originally made 3 mm diameter and 1 cm.long, but the diameter has been increased to 5-7.5 mm in order to decrease pressure drop. The larger particles are apparently satisfactory.

The reactor base and tubes are filled with porcelain raschig rings for about 6" up the tubes and another 6" layer is added at the top of the tubes. The reactors are equipped with thermocouples inserted through the top in order to measure reaction temperature and vapor distribution. The reactors are dumped by lifting off the top, pulling out the rest of the metal part of the reactor, including tubes, headers, baffle plates and base. The base is then removed and catalyst removed.

The reactor products after being cooled in heat exchange to 320° are sent to a precooler and condenser from which the condensate leaves at 40°. The gas is further cooled, first with water and then brine to 2° to knock out condensibles. The liquid condensate from the condenser goes to a separator to remove water and then to a small stirred vessel where 0.005-0.01% hydroquinone is added. The condensate from the water and brine aftercoolers is added to the crude styrene at this point. In winter a drier is inserted to prevent ice formation. About 40-50 m^3 of gas is produced per 100 kg styrene and the average analysis is 80-85% H_2, 10-12% CO_2, 1-2% C_2H_4, 1-2% CH_4, 0.5-1% CO, 0.5. - 1% O_2 and remainder N_2.

Styrene Purification.

The initial purification of styrene takes place in five separate parallel trains for the preparation of crude styrene, each of which consists of two bubble towers in series. The crude styrene is then purified in three pure styrene columns in parallel two of which are packed towers and one of which is a bubble tower. One further plate column is used for the distillation of condensate from brine coolers, and there are two flashers for the working up of residues from the pure styrene stills. Each of the five crude styrene trains has a capacity of 700 T styrene per month and each of the three styrene stills has a capacity of 2,000 T/Mo. Provision for a sixth distillation train for crude styrene had been made, but no equipment was on hand.

The first crude styrene tower contains 45 plates and is 2.0m. in diameter. The feed from the reactors, containing 38% styrene and 1.1/2 - 2% benzene and toluene enters on the 9th to the 21st plate from the bottom. The tower operates at 25-30 mm top pressure, 175-185 mm bottom pressure, 40-45° top temperature, 95 - 105° bottom temperature and 3-5 reflux ratio. From the top of the column is taken ethylbenzene containing 0 - 2% styrene which is condensed and returned to dehydrogenation. From the base of the column is taken a stream of 80% styrene, 20% ethylbenzene, which is fed to the second crude styrene tower.

The five second crude styrene towers consist of three of 24 plates each and two of 28 plates each. The bottoms from the first crude styrene tower is sent to the 11th - 21st plate of the second tower, which is 2.0m in diameter and which operates at 8 : 1 reflux ratio. The top pressure is 15 - 20 mm, and the temperature 35 - 40°. The bottom pressure is 70 - 75 mm and the temperature 80 -85°. From the top of this column is taken a stream of 40% styrene, 60% ethylbenzene, which is returned near or at the feed plate of the first column. From the base of the second column is taken a crude styrene for feed to the pure styrene stills. This has an indicated concentration of 102% styrene, based on refractometer tests.

The gases from the first tower go to a brine cooler where the temperature is dropped to 5°. The condensate, containing 75% ethylbenzene and 25% benzene-toluene is taken to a batch bubble column 1.0 m in diameter and containing 60 plates where the material is distilled at atmospheric pressure, 12:1 reflux ratio, 100° top temperature and 140° bottom temperature to remove benzene-toluene overhead and recycle ethylbenzene from the bottom. The benzene-toluene is sent to another plant for purification.

The gases from the second crude styrene column go to a separate brine cooler and the condensate is returned to the feed plate of the first column along with the overhead from the second column. It is emphasized that the two columns were used in order to prevent too high bottom pressures and corresponding bottom temperatures which would cause styrene polymerization if only one tower were used. By using 0.01% hydroquinone in the feed, keeping the temperatures low, and by having a very small liquid level in the towers polymer formation is prevented.

The crude styrene from the five sets of two columns each is then sent to three parallel pure styrene stills. One of these is 1.6 m diameter and contains 20 plates; the other two are the same size, but packed with raschig rings. The crude styrene is fed to the 7th - 15th plate, and by operating at o.3 - o.5 reflux ratio, 10mm top pressure, 45-50 mm bottom pressure, 35° top temperature and 80-85° bottom temperature a 99.5 - 99.7% styrene is produced overhead. The gases from the top of the column go to a brine cooler and the condensate is returned to the feed of the first towers in the crude styrene train.

The residue from the pure styrene stills is sent to two strippers in parallel. The feed is about 50% styrene and 50% residue containing stilbene, diphenyl compounds, etc. The strippers are 1.0 m. in diameter. The overhead from the stripper is styrene which is returned to the feed of the pure styrene columns. The residue is sent to two stored vessels 1.4 m in diameter where residue from the ethylbenzene stills is added to make the material fluid. The mixture is then removed and worked up into a rubber extender.

It was emphasized that a very high purity of ethylbenzene must be used in this process, free from diethyls, or divinyl compounds are formed which accelerate polymenization due to cross-polymenization in the towers. The styrene towers are also tinned on the inside and the towers washed every two months to remove salt accumulations.

The towers are located so the bottom six plates can be readily removed, if necessary. It is claimed, however, that polymer deposition has been negligible.

The overall yield of styrene from the process is stated to be 90% of theory. In addition there is produced 3-4% benzene-toluene and 1.1/2% residue. The reactors themselves give a yield of 90 - 96% and the distillation losses amount to about 2%.

The side reactions in the process are due largely to the formation of stilbene, toluene, methane, etc. by thermal cracking. Styrene also will split off CH_2, form stilbene and the CH_2 reacts with H_2 to form Methane. Diphenyl is formed from benzene and various alkylated diphenyl compounds are also produced. Care in using pure ethylbenzol, using Cu- Mn lined tubes and maintaining a uniform catalyst temperature is necessary in order to obtain high yields.

Analysis of Styrene.

The following tabulation shows typical analyses and specifications for styrene for use in buna manufacture.

	Typical	Specification.
% styrene by bromine method	99.5-100%	99.0% min
% " " refractometer	99.4-99.8%	
% p-divinylbenzol	0.001%	0.005% min.
% hydroquinone	0.01% *	-

* only for styrene shipped out.

1. Bromine method for styrene determination.

A 0.1 normal bromine solution is prepared by saturating 2 liters of methanol with dry sodium bromide and reacting this with 79.92 gms of bromine. The solution is checked daily.

2.5 - 3.0 gms of styrene are dissolved in 250 cc of dry methanol. 25 cc of this solution is reacted with 15.0 cc of the bromine solution in an Erlenmeyer flask. This is allowed to stand in the dark for 10 minutes. 20 cc of 10% potassium iodide solution is added and titrated with 0.1 normal thiosulfate solution in the presence of starch solution until colorless. The bromine solution is standardized by taking 15.0 cc of solution, 100 cc of H_2O and 25 cc of methanol and potassium iodide solution.

If E is the grams of styrene, a the c.c of thiosulfate used for titration of the sample and b the cc of thiosulfate used for standardization the % styrene is given by

$$\% \text{ styrene} = \frac{(b-a) \times 5.203}{E}$$

11. Refractometer method for styrene determination.

This method is to determine the % styrene by determining the refractive index at 20° and comparing with the index for styrene ($n_d^{20} = 1.54669$) and for pure ethylbenzol ($n_d^{20} = 1.49596$), assuming the impurity to be ethylbenzene and drawing a straight line relationship of refractive index versus % styrene.

Determination of hydroquinone.

10 cc of styrene is agitated for one minute with 20 cc of 10% ammonia solution. After settling the red colored layer is studied in a Pulfrich step-photometer using a S50 filter in a 30 mm cell. The extinction is a measure of the hydroquinone content.

PRODUCTION OF BUNA POLYMERS AT THE HULS CHEMISCHE WERKE

I. Summary.

Four types of Buna rubber were made at the Hüls Chemische Werke - namely Buna S, SS, SR and S 3. Total rated capacity for the production of these polymers was about 50,000 long tons per year.

Polymerization was carried out continuously in eight lines of six reactors each. Latex finishing operations, including coagulation, filtration, drying, etc. were conducted in nine lines; six in Bldg.259 and three in Bldg.184. The lines in Bldg. 184 were put out of operation by bomb damage the week of March 25, 1945.

The Buna polymerization process employed at Hüls is described briefly below:

Fresh butadiene and styrene were premixed and then emulsified with Emulgator solution containing Nekal BX (sodium salt of di-isobutyl naphthalene sulphonic acid), caustic soda and linoleic acid (for Buna S, SS and SR) or paraffin fatty acid (for Buna S 3). The mixture was pumped continuously through five of the six reactors at about 45°C. Potassium persulfate was added as reaction activator to the first vessel. Di-isopropyl xanthogen disulfide (only in the case of S 3) was also pumped to the 1st, 3rd and 5th vessels. The reaction was carried to 57-60% conversion, phenyl-beta-naphthylamine being added to the latex leaving the fifth reactor. Charge recipes for all types of rubber are given later in this report. Reaction times were about 30 hrs.

The latex was then steam stripped counter-currently under vacuum in two stepsto remove unreacted monomers. Styrene and steam vapors leaving the unit were condensed and the styrene was separated by decantation. Butadiene gas was compressed and then liquefied by cooling. Both hydrocarbons were redistilled prior to re-use in the polymerization process.

Stripped latex from the recovery unit was blended in largetanks from which it was eventually pumped to the finishing building. Here it was creamed with brine in one pipe tee and coagulated with sodium bisulfite solution in another tee which followed in the line. A small amount of

$FeSO_4$ solution was also added to Buna S 3 latex during coagulation. Ferrous ions in the polymer were said to catalyze subsequent thermal breakdown.

The fine crumb which was obtained by coagulation was filtered from serum on a paper-machine screen (Fourdrinier type). The resulting blanket was washed, squeezed and then dried at about 110-130°C. The sheet was dusted with talc and rolled into 100 Kg. bundles for shipment.

Some Buna latex (Igetex) was concentrated to about 50% rubber content at Hüls for use in cord dipping and cloth impregnation. The method involved (1) beating the latex to foam by special vigorous agitation, and (2) simultaneously cooling this foam to the "Stockpunkt" or thickening temperature. Some Na_2CO_3 was usually added to the latex to raise the Stockpunkt and improve the thickening action. During the foaming and cooling stages, latex particles agglomerated; and on standing, separated from substantially clear serum as a layer of concentrated latex.

II. Polymerization of Buna Rubbers.

A. Raw Materials.

1. **Butadiene.** Butadiene is pumped from the manufacturing plant to underground storage tanks outside of the polymerization buildings. The purity usually runs about 98.5-99%. No inhibitor is added to the butadiene, but a layer of NaOH solution is maintained in the tanks to destroy polybutadiene peroxides which settle out as fine, oily droplets. Butadiene is pumped from the storage tank through a dip leg so that it is not contaminated with caustic.

As required, butadiene is pumped to a 50 cubic meter blending tank and mixed with the proper quantity of styrene. The volume charged to the blend is metered and also gauged by level changes in the tanks involved. Four such blend tanks serve the polymerization lines so that several types of latex can be prepared simultaneously.

2. **Styrene.** Styrene of 99.5% or higher purity is likewise supplied by the manufacturing plant without any stabilizer. If it is to be stored for a considerable time, about 0.01% hydroquinone is added by means of small portable charge tanks. Styrene is pumped by centrifugals to the 50 cubic meter mixing tanks along with butadiene as described above. The monomers are carefully metered to give the

desired blend. Final mixtures are usually analyzed, and corrected if necessary to within 1% of the desired concentration. Mixing is effected by recirculation through a head tank, which provides constant inlet pressure to the reactor charge pump.

3. Recycle Hydrocarbons. Unreacted monomers recovered from latex are redistilled and blended with fresh material as required. Anywhere from 5-30% by weight of 95% purity recovered butadiene, for example, may be mixed with fresh butadiene for use in polymerization. Average purity of this butadiene feed is about 98%. Fresh styrene is mixed with 94-96% purity recovered styrene in a similar manner.

4. Emulsifier Solution. Nekal BX, which is used for emulsifying the hydrocarbon phase, is said to be a mixed di-isobutyl naphthalene sodium sulphonate made up as a 30% solution in water. The solid Nekal itself is 65% soluble ~~in ether (active ingredient), the remainder consisting of NaCl~~ and Na_2SO_4. The water solution is called Emulgator 1000 and is prepared in one of four 50 m^3, tile-lined, insulated tanks.

To this solution is added either (1) linoleic acid (for Buna S, SS and SR), or (2) paraffinic fatty acid (for Buna S 3), plus caustic soda for saponification. Usually an excess of NaOH is added so that the pH of the reactor emulsion is 10-12. Softened boiler feed water is used for dilution of the Nekal.

Contents of the emulgator tank are mixed by circulating with a centrifugal pump. A head tank located in the circulation line gives constant feed pressure on the charging pump. The mixture is heated by live steam, so that the emulsifier may be charged hot.

5. Fatty Acids. When linoleic acids grew scarce in 1944, it was necessary to manufacture a modified polymer, now termed Buna S 3. Since linoleic acid was believed to act as a regulator during polymerization of the original Buna S, and as a stabilizer during heat plasticization, it was necessary in Buna S 3 to obtain similar results with substitute materials. This is accomplished by including (1) Diproxid for regulation of the molecular structure, and (2) paraffinic fatty acid to

provide the stabilizing action during heat softening. The resulting polymer is considered by the Hüls management to be better than the original Buna S.

Paraffinic fatty acid is prepared by the Witten Fettsaürewerke through oxidation of paraffin oils obtained from Fischer-Tropsch plants. It consists of a range of C_{10} - C_{15} fatty acids.

6. Catalyst Solution. Buna polymerizations at Hüls are catalyzed by potassium persulfate ($K_2S_2O_8$). The catalyst is pumped continuously as a 3-4% solution to the hydrocarbon emulsion line entering the first reactor. V_2A alloy (18-8 Cr-Ni) is used for pipe lines, the pump being VA metal. Solutions are prepared in a rubber -lined(Buna S) vessel, and stored in plastic-coated feed tanks.

7. Modifier. Di-isopropyl xanthogen disulfide is used to modify or regulate the molecular structure of polymer in the Buna S 3 process. It is called Diproxid by the Germans. The average consumption is 0.1% per 100 parts of hydrocarbons, which represents about the most that can be used to obtain desired tackiness and softness, without sacrificing the overall polymer quality. Greater concentrations of Diproxid tend to retard the polymerization, in addition to giving a less desirable product.

In other Bunas, as already mentioned, linoleic acid apparently provides the necessary modification and stabilizes the polymer during subsequent heat treatment.

Diproxid is made up as a 5-10% solution in styrene in an agitated vessel. From here it is blown with nitrogen to several groups of calibrated feed tanks. About 0.03% per 100 parts of hydrocarbons is charged by positive displacement pumps to each of the 1st, 3rd and 5th reactors. Piping is so arranged that the modifier can be pumped to any combination or to all of the reactors. It was stated that the polymerization tended to be retarded if all of the modifier were added to the first reactor. The Diproxid feed rate is hand regulated and checked by flow from the calibrated feed tanks.

B. Polymerization Operation.

1. Charge Formulas. Charge formulas for the various types of rubber manufactured at Hüls are given in the table below:

Material	Buna S	SR	SS	S 3
	(Parts/100 parts of Monomers)			
Butadiene	68	68	47	68
Styrene	32	32	53	32
Emulgator (Nekal)	2.85	2.85	3.2	3.1
Linoleic Acid	2	2	2.5	-
Paraffinic Fatty Acid	-	-	-	0.5
NaOH	0.44	0.44	0.55	0.32
Diproxid	-	-	-	0.09
$K_2S_2O_8$	0.46	0.46	0.61	0.45
Water	120	120	182	105

All polymers described above are prepared at 45-50°C, except Buna SR. This type is composed of a 50/50 mixture of Buna S and Buna R (rapid), which latter type is reacted in the following manner: Buna S recipe and conditions are maintained through four successive reactors; but temperature in the fifth reactor is held at 80-90°C. Conversion of Buna R reaches 96% under these conditions.

2. Equipment. Polymers are produced continuously in eight lines of six 20 m^3 reactors. Only five vessels of each line are used for reaction, the sixth being considered stand-by so that repairs or cleaning can be made without interrupting production. Reactors in Bldg. 241 are constructed as follows: three lines are lead-lined steel; two are chromium-plated steel; one is V_2A steel. Reactors in both lines in Bldg. 188 are also made of V_2A. Enamel or glass linings were not used because of low heat transfer coefficients.

Reactors are agitated with VA metal stirrers, consisting of three horizontal paddles mounted at the top, middle and bottom of the shaft. Agitators are run at 30 RPM by 8 amp., 500 volt motors. The stirrer stuffing box is lubricated with "Autoco" grease, which is similar to Merco-Nordstrom valve lubricant. No leakage of this material into reactors was reported.

Reactors are pressure tested at 25 atm., have a design operating pressure of 15 atm., but are usually run at 8 atm. They operate full of liquid, pressure on the units being hand-controlled by a valve in the outlet latex line.

Although the flow of hydrocarbons and Emulgator to the reactors is manually controlled in most of the German polymerization plants, special design, recording flow controllers are installed on the two reactor groups in Bldg. 188. This automatic control equipment operates as described below.

Standard nutating-disc displacement meters (Taumelscheiben Zähler) are located in the feed lines in the conventional manner. However, in place of the simple mechanical counter, there is installed a combination counter-tachometer - generator assembly. As usual, the counter registers total cubic meters handled. The tachometer needle indicates instantaneous flow rate on a round dial graduated from 0-12 m^3/minute. Current delivered by the generator is conveyed to the new recording-controlling instrument on the main panel board. This instrument operates as follows: Flow rate through the meter is recorded on a strip chart by a pen connected to a galvanometer, activated by current from the meter generator. On a central pointer, which can be set to the desired rate, is mounted a small hot wire. This is heated by a constant 20 m.a., 6 V current. On the recording pen arm is affixed a black vane, which travels in a plane parallel to the hot wire. As the recording pen starts to coincide with or pass the control set pointer (and the hot wire), heat is absorbed by the black vane, causing the wire to contract. Expansion and contraction of the wire operates a small air valve which varies pressure on a control diaphragm. This in turn governs the air pressure on the diaphragm operating the reactor feed motor valve. Control accuracy is considered to be ± 1%.

Screens are installed in all feed lines ahead of meters to reduce meter maintenance. Basket-type screens are also employed to filter coagulum from latex leaving the final reactor.

The temperature of river water used in reactor jackets and condensers is lowered from 25-28°C to 11°C by two-stage condensing vacuum jets.

G. **Procedure.** The Emulgator solution and hydrocarbon blend are pumped continuously in the desired ratio into 200 gal. turbo-mixed emulsifying vessels, located at the head of each line of reactors. In Bldg. 241, proportioning (piston) charge pumps are used, flow rates being continuously indicated by means of the nutating-type meters. Correct rates are maintained by hand control.

In Bldg.188, centrifugal charge pumps (Siemen & Hinsch) are employed. Flow rates are metered as well as automatically controlled by a special instrument, which has been discussed in the preceding section on equipment.

As previously described. the catalyst is pumped into the first reactor to initiate polymerization. In Buna S 3 preparation, Diproxid is also charged into three of the vessels (1st, 3rd and 5th) by means of small piston pumps.

Approximately 1500 kg. of hydrocarbons and 1800 kg. of aqueous phase are charged each hour for the production of Buna S. Based on this feed rate and the volume of five vessels (100 m^3), a hold-up or reaction time of 30 hours is indicated. Because more water is included in the Buna SS recipe, the hourly feed rate of hydrocarbon phase must be reduced somewhat. Whereas the polymer yield rate of Buna S at 60% conversion is 9 $kg/m^3/hr.$, for Buna SS it is therefore only 8 $kg/m^3/hr.$ On the basis of the latter production rate, the reaction time for Buna SS is calculated to be about 27 hours. Reaction times reported by Hüls personnel (25-30 hours) are in good agreement with the values estimated above for Buna S and SS.

Reactor temperatures are recorded continuously, but must be regulated by hand control of the jacket cooling water. Polymerizations of most Buna types are ordinarily conducted at 45-50°C. Buna R, however, is reacted at about 45°C in the first four vessels, and is allowed to polymerize at 80-90°C in the last stage. This temperature is reached and maintained, since no cooling water is applied to the final reactor. Conversion progresses at this point to about 96%, whereas 57-60% final conversion is normal for Buna S, SS and S 3. Buna SR is a 50/50 mixture of Buna S and Buna R, blended in the latex state.

Previous to the last quarter of 1944, Buna R was made by by-passing the last reactor, cutting off its cooling water and allowing it to operate batchwise to essentially complete conversion. Temperature rose to 80-100°C in the course of about four hours' additional polymerization. The present method of continuous operation gives better control and more uniform quality.

The following table shows approximate conversions by reactors in the continuous production of Buna polymers at Hüls :

Buna Type	% Conversion in Reactors 1	2	3	4	5
S	20	35	44	52	57
SS	20	36	45	54	60
R	15	25	32	40	96
S 3	20	35	44	52	57

Since the reaction rate of Buna R was greatly accelerated by high temperature in the last reactor, it was apparently possible to operate the line at a greater throughput than normal. This would explain the lower conversion values shown in the first four reactors.

Polymerizations are followed by a coagulation control test which indicates hydrocarbon conversion. In brief, 50 g. samples of latex are coagulated with 300 cc. of a methanol-$CaCl_2$-acetic solution.* Conversions are calculated from the weight of washed and dried coagulated polymer (corrected for nonhydrocarbon constituents). It was reported that each reactor in a line was checked in this manner every four hours. The combining ratio of butadiene/styrene is determined as desired by steam distillation of 50 g. of latex.

Reactors are usually opened every three to six months for removal of polymer film. When a vessel is ready to be cleaned, it is by-passed; the reaction is allowed to complete batchwise; and then latex is blown out with nitrogen. Conventional cleaning procedure is used. Film build-up in the V_2A reactors was stated to be considerably less than in lead-lined equipment.

Latex from the last reactor is filtered to remove precoagulum. Filters are cleaned weekly. The latex is

* 900 cc. of CH_3OH, 50 cc. conc. $CaCl_2$, 50 cc. H_2O, 3 cc. conc. acetic acid.

then stabilized by addition of 3% phenyl-beta-naphthylamine, ~~based on the rubber. Until January 1945,~~ the powdered PBNA was made up as a 20% dispersion in aqueous Nekal. Because of considerable difficulty with plugging of the latex feed line to the recovery unit, which was caused by precipitation of the PBNA, recent practice has called for the addition of the stabilizer as a 17% solution in styrene.

III. Monomer Recovery.

A. Stripping Operation. Unreacted butadiene and styrene are recovered from latex by steam stripping under vacuum in two steps. Latex is fed to the top of a short tower (step 1), where steam coming from the second stage (described later) is also introduced. The mixture passes downward over a series of baffle plates, where the monomers are vaporized. Considerable foaming occurs at this point. ~~The foamy latex is discharged through a constricted opening~~ at the bottom of the column into a large flash chamber. ~~Because of its relatively high velocity through this~~ opening, the foam is broken down.

Butadiene and styrene vapors separate from the latex at this point and pass through an entrainment trap for removal of latex carry-over. The trap was said to be filled with 1" x ¼" iron strips in order to obtain a maximum of surface.

Latex from the first step is transferred to the top of a second smaller tower by means of a simple steam-lift ("Mammut Pumpe"). Fresh low pressure steam is also injected at the top of this tower to strip off the remaining styrene to a concentration of 0.1% by weight. Stripped latex is separated from the vapors in a flash tank situated at the bottom of the column. The overhead steam, which contains some styrene, is used for stripping latex in the initial flashing step previously described. The whole unit operates at 100-120 mm. Hg pressure. Vacuum is obtained by a Siemen Elmo (water sealed) pump.

Stripped latex runs from the second flash tank to a barometric-seal vessel, and then to four 20 m^3 intermediate storage tanks.

IV. Finishing Operations.

A. Solution Preparation. Buna latex is transferred from storage tanks at the polymerization building to four 150 m^3 jacketed, agitated blend tanks at the finishing building. (In the discussion following, references are made to the equipment in Bldg. 259). It is circulated through 8 m^3 constant head tanks provided for each coagulation line by means of "Kanalrad" pumps (two-bladed impeller centrifugals). A filter screen in the circulation line removes dirt or precoagulum.

On the same level as the constant head latex tanks are located the following solution tanks, which serve six coagulation lines:

1 - 10 m^3 for 11% brine.
2 - 10 m^3 for 40% sodium bisulfite.
~~1 - 8 m^3 for 0.34% ferrous sulfate.~~
1 - 20 m^3 water storage.

Tanks for the first three solutions are rubber-lined.

Brine is prepared from rock salt as a saturated solution in pits next to the finishing building. Insoluble residue in the brine is reduced to less than 1, by filtering through a 30 cm. layer of sand supported on a coke filter plate. Recently a natural brine obtained from the Auguste Viktoria mine at Hüls has been used in place of rock salt. Its composition is approximately : NaCl - 120 to 125 g/l; $CaCl_2$-15 to 18 g/l; $MgCl_2$- 4 to 6 g/l; and $BaCl_2$- 0 to 2 g/l.

Sodium bisulfite is dissolved in two 50 m^3 tanks, and the resulting solution is pressured into the 10 m^3 vessels listed above. Analysis of the solution shows: $NaHSO_3$ - 40.6%; SO_2 - 0.5%; Na_2SO_3 - none; pH - 4 to 4.5 (100 g. of solution consume 15.9 g. of NaOH); and Fe - 10 to 150 mg/l. Formerly, acetic acid was employed for coagulation, but when it became scarce, it was necessary to use $NaHSO_3$. Trials with H_2SO_4 led to excessive corrosion troubles.

Ferrous sulfate solution is prepared by dissolving 65 kg. of $FeSO_4 \cdot 7\,H_2O$ in 10,000 l. of water in a cellar tank. It is pressured to the upper 8 m^3 storage tank as needed.

B. Coagulation. Latex, coagulants and dilution water flow by gravity to a 2½" glass coagulation pipe containing two special tees. Latex flow is hand-controlled and is measured by a calibrated Venturi (silvered-throat) flowmeter. Temperature of the latex is held at 30-40°C, since the higher the temperature, the more "curdy" and difficult to dry will be the rubber particles. Flow of brine, bisulfite and water is metered by rotameters. The coagulation unit is designed so that both coagulant streams may be diluted by measured amounts of water.

Latex enters the first tee, where it is given a twirling or spiral motion by an internal nozzle. Brine runs into the side of the same tee, directly opposite the tip of the nozzle, and creams the latex. The creamed latex travels about 24 inches and enters the second tee, which is exactly the same as the first. Here, $NaHSO_3$ solution is injected and coagulation to fine particles occurs. The resulting slurry is diluted with recycle serum and/or water just before it enters the bottom of a distribution box feeding the filter. Buna SS is diluted more than the other types during coagulation (to 15% solids) in order to obtain proper crumb size.

Although specific data concerning the use of $CaCl_2$ in creaming Buna S 3 latex were not obtained, it was reported that both $CaCl_2$ and NaCl were added during Buna S 3 coagulation. S 3 latex was said to be more stable and therefore required the divalent calcium ions to ensure flocculation to the proper particle size. Production data given in Section V A show a usage of 10.1 kg. of $CaCl_2$/100 kg. of Buna S 3 in addition to 38.4 kg. of NaCl and 11.4 kg. of $NaHSO_3$.

In the production of Buna S 3, $FeSO_4$ solution is also added during the coagulation step. Fe^{++} ions are claimed to catalyze thermal breakdown of this particular rubber, so $FeSO_4$ is added in an amount equivalent to 130 g. of Fe^{++} per 1000 kgs. of Buna S 3. This is roughly equivalent to 0.07 kg. $FeSO_4 \cdot 7\ H_2O$/100 kg. Buna S 3.

C. Filtration. Rubber particles are filtered from serum on an endless paper-making screen (Fourdinier type) which should be made of Nickel, Monel, or V_2A metal.

Because of a nickel shortage, screens at Hüls were fabricated from V_2A ("Silvereen"). The resulting sheet is washed and pressed by rolls to about 55% moisture content. It is important that a fine floc be formed during coagulation so that good washing and thorough drying will be possible. It was stated that of all things, it is very essential that the Nekal be washed out. In this connection, not more than 0.15% sulfur ought to be in the dry band. Both ash and moisture should be under 1%.

During normal operation, a 3-4% loss of Buna occurs in the filtration and drying steps. This "clean-up" material is reduced to crumb form and is squeezed to an average moisture content of 17-18% in a Krupp press. The resulting crumb is dried on a hot plate and is packed in sacks for shipment.

D. Drying and Rolling. The sheet or band of rubber from the Fourdrinier is dried continuously in a circulating air dryer. The sheet averages about 2.5 mm. in thickness and travels at 6.5 meters per minute. In Bldg. 259, the dryers contain 15 heating passes and two passes for atmospheric cooling. Passes are 17 meters long. The heating section of the dryers is divided into three zones which are maintained at successively lower temperatures, lying between 100-130°C. The dryers in Bldg. 184 contain 17 - 20 meter passes for drying, and two for cooling, permitting higher operating rates.

The rubber sheet from the dryer is powdered with talc, and is rolled into 100 kg. bundles. Two separate talcing-roller mechanisms mounted on scales are provided for each line.

E. Finishing Rates. As an example of typical Buna S coagulation and drying operations, the following data from a report of April 23, 1945 by Dr. Knoche are presented:

Production rate	1000 kg/hr
Latex	3500 l./hr (approx.)
Brine (11%)	3600 l./hr
Water	2000 l./hr (dilution)

(cont'd)

Bisulfite (40%)	100 l./hr	
Water	3000 l./hr (dilution)	
Wash Water	1500 l./hr	
Dryer temperatures:	1st zone	130°C
	2nd zone	121°C
	3rd zone	117°C
Talc	7.0 kg/hr	

Previous verbal information obtained from Dr. Baumann indicated that for 1000 kg/hr of Buna S (about 3500 l/hr latex), the following amounts of materials were necessary for coagulation:

Brine (23%)	2000 l/hr
Water	2800 l/hr (dilution)
$NaHSO_3$(35°Be)	60 l/hr
Water	6000 l/hr (dilution)
Dilution Water	6000 l/hr
Wash Water	8300 l/hr.

It is evident that the two sets of data are not entirely consistent. However, since the latter figures were obtained by interrogation, it is believed that the former summary is the more dependable.

Further data related to the Buna finishing operations were found on a rough flow sheet prepared by Dr. Meis. Figures are given below:

Buna Production	Wash Water	Steam	Power
Sept. 1944 - 2940 tons	284,000 m^3	7440 tons	@ 250,000 Kws
Oct. 1944 - 2500 tons	241,000 m^3	7460 tons	@ 250,000 Kws

F. <u>Product Control.</u> Buna rubber coming from the production lines at Hüls is sampled about once every two hours. Samples are subjected to routine physical tests which will be described in a separate report. One of the principal tests conducted on the raw polymer involves determination of the Defo Number. This test indicates the plasticity or softness of the stock. Defo Numbers on the average fall within 10% of the following values: Buna S - 5,000, Buna SS - 4500 and Buna S 3 - 3000. Since the Defo can be adjusted to the desired range by subsequent heat treatment, no effort is made to control the raw Defo rigidly.

Normal ranges of analysis for Buna S and Buna SS are tabulated below :-

	BUNA S %	BUNA SS %
Total hydrocarbon [x]	@ 94	@ 93
Butadiene[xx]	80-77.5	60-57.5
Styrene[xx]	20-22.5	40-42.5
Ash	0.3-0.8	0.3-0.8
Polystyrene	0.1-0.4	0.4-1.0
Linoleic Acid	3.5-4.0	3.5-4.0
Nitrogen	0.12-0.18	0.12-0.18
Iron	0.002-.012	0.002-.015

[x] Total hydrocarbon in S 3 is about 96%

[xx] Calculated on the ash free sample.

It was reported that the combining ratio of butadiene to styrene in the polymer was calculated from determination of the double-bond content.

V. Miscellaneous.

A. Buna Production Data. In the table below are summarized quantities of raw materials consumed in the manufacture of Buna rubbers at Hüls:

Polymerization
Parts/100 parts of Hydrocarbons in the Polymer[x]

Material	BUNA-S	-SS	-SR	-S 3
Butadiene	73.9	52.6	74.3	72.8
Styrene	26.1	47.4	25.6	27.2
Linoleic Acid	3.7	3.8	3.0	--
$K_2S_2O_8$	0.8	0.78	0.7	.65
NaOH	0.68	0.80	.63	.66
Emulgator 1000	4.3	6.3	3.0	5.3
Paraffinic Fatty Acid	--	--	--	.87
Diproxid	--	--	--	.12
PBNA	2.5	2.4	3.9	2.2
HQ[xx]	0.01	0.01	0.01	0.01

[x] Average for 1944.

[xx] For inhibiting polymer formation in the recovery unit.

Finishing
Parts/100 parts of Polymer[a]

Material	BUNA -S	-SS	-SR	-S 3[b]
NaCl	35.4	23.8	27.1	38.4
$NaHSO_3$	6.9	7.3	6.9	11.4
$CaCl_2$	-	-	-	10.1
$FeSO_4$	-	-	-	0.1
Talc	0.8	0.8	0.8	1.0

[a] Average for 1944.

[b] Data for third quarter 1944 only.

Owing to changes in operation dictated by bomb damage and the usual process developments, the raw materials usages given above perhaps do not give an exact picture of operations. For that reason, more detailed data are given by quarters in the tables on the following pages.

It is evident that appreciable changes took place during 1944 especially in the requirements for Buna S 3, the newest polymer. The coagulation picture of Buna S 3 is especially confusing, which probably indicates that the process was being continually improved since its adoption early in 1944;

Utilities requirements for Buna S and Buna SS were obtained from Dr. Baumann during interrogation at Hüls. Based on production of 1700 tons per month of Buna S and 1300 tons per month of Buna SS, the following utilities were required :

Raw Material Usages in Kg. per 100 Kg. of Rubber.

Material	1942	1943	Quarter in 1944 1	2	3	4	1944 Av.
				BUNA S			
Butadiene	79.8	77.7	76.8	76.6	76.2	75.5	76.4
Styrene	30.1	28.2	27.8	28.6	25.8	27.6	27.2
Linoleic Acid	3.8	3.5	3.5	3.6	3.9	3.3	3.6
Emulgator	7.8	7.5	4.2	4.4	4.4	3.6	4.3
$K_2S_2O_8$	0.7	0.7	0.7	0.8	0.7	0.7	0.7
NaOH	0.8	0.7	0.7	0.7	0.7	0.6	0.7
PBNA	3.3	2.9	2.3	2.6	3.1	2.8	2.6
NaCl	56.9	58.1	42.3	43.9	32.5	22.8	38.2
$NaHSO_3$	2.6	7.6	6.8	7.1	8.0	5.5	6.9
				BUNA SS			
Butadiene	59.4	57.2	56.4	56.8	56.8	56.1	56.6
Styrene	56.7	54.4	53.3	54.0	48.9	47.8	51.6
Linoleic Acid	4.0	3.9	3.9	3.9	4.6	3.5	4.0
Emulgator	11.7	11.1	6.8	6.8	6.8	6.0	6.7
$K_2S_2O_8$	0.9	0.9	0.9	1.0	0.9	.6	0.9
NaOH	9.9	0.8	0.9	0.9	0.9	.8	0.9
PBNA	3.3	2.8	2.2	2.3	3.3	2.5	2.5
NaCl	78.8	98.4	73.3	25.7	21.8	23.9	41.5
$NaHSO_3$	7.4	0.5	8.2	7.9	8.1	5.9	7.8

Raw Material Usages in Kg. per 100 Kg. of Rubber

Material	1942 Av.	1943 Av.	Quarter in 1944: 1	2	3	4	1944 Av.
BUNA SR							
Butadiene	78.1	77.4	77.2	73.9	75.0	75.4	75.4
Styrene	33.0	31.9	30.6	30.8	27.3	25.4	29.9
Linoleic Acid	3.0	2.8	2.9	2.9	3.5	3.7	3.0
Emulgator	5.7	5.6	3.6	3.9	4.4	4.8	3.9
$K_2S_2O_8$	0.6	0.6	0.6	0.6	0.7	0.8	0.7
NaOH	0.7	0.6	0.7	0.7	0.7	0.7	0.6
PBNA	3.2	2.9	2.0	2.4	4.8	3.1	2.5
NaCl	63.6	63.1	39.8	36.0	34.8	37.8	37.5
$NaHSO_3$	7.0	7.3	8.0	8.4	7.7	3.4	7.7
BUNA S 3							
Butadiene	-	-	-	90.3	84.1	79.7	81.5
Styrene	-	-	-	35.5	30.2	29.4	29.9
Paraffinic fatty acid	-	-	-	1.4	0.8	0.8	0.8
Emulgator	-	-	-	6.1	5.9	5.7	5.8
Diproxid	-	-	-	.13	.10	0.16	0.14
$K_2S_2O_8$	-	-	-	1.0	0.6	0.8	0.7
NaOH	-	-	-	1.1	0.7	0.6	0.7
PBNA	-	-	-	3.2	2.1	2.7	2.5
NaCl	-	-	-	51.8	38.4	4.5	17.1
$CaCl_2$	-	-	-	25.8	10.1	2.2	5.7
$NaHSO_3$	-	-	-	8.7	11.4	10.2	10.5
$FeSO_4$	-	-	-	-	0.1	0.04	0.06

	BUNA S	BUNA SS
Process Water	230 m^3/ton	250 m^3/ton
Steam	3.3 t/ton	3.5 t/ton
Electricity	145 Kwh/ton	165 Kwh/ton
Nitrogen	13 m^3/ton	16 m^3/ton
Air	7.5 m^3/ton	8.5 m^3/ton
Treated Water	1.8 m^3/ton	2.0 m^3/ton

It was reported by the Hüls management that production rates (for one line) of the Buna rubbers varied in the following manner :

BUNA S	1000 kg/hr	600 tons/mo.
SS	800 "	480 "
SR	850 "	510 "
S 3	750 "	450 "

Operations are based on a 600 hour month, the remaining time being consumed by repairs and cleaning of equipment. It was reported that hourly production of Buna S 3 could be raised from the figure listed above.

B. Concentration of Buna Latex.

1. Introduction. In the investigation of synthetic rubber production at Hüls, a procedure for concentrating latex to approximately 50% rubber content by weight was disclosed. The method involves beating latex to foam by vigorous agitation while simultaneously cooling it to the "stockpunkt" or thickening point. The "stockpunkt" has been defined by the Germans as the temperature at which the latex dispersion becomes so rigid or viscous that it does not further flow under the action of gravity. The method appears to be applicable to most Buna latices, natural rubber latex, polystyrene emulsions and other aqueous dispersions of high molecular weight substances.

Development of the concentrating equipment has been underway for over 5 years. The latest batch type vessel which is described later in this report was installed at the Hüls chemische Werke. It was indicated that a continuous concentration unit was being designed.

Advantages shown for this concentration method were as follows: (1) It is rapid; (2) it is simple and practicable; (3) the stability of the dispersed product

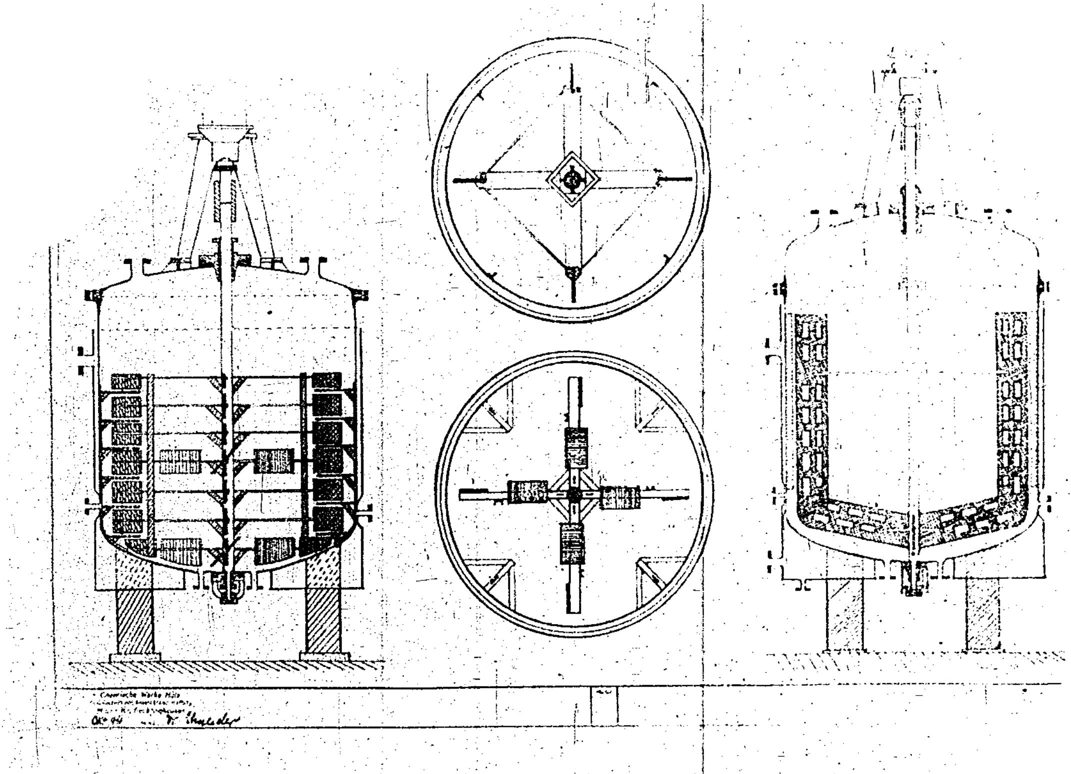
~~is not influenced; (4) it is applicable to all types of~~ aqueous dispersions of high molecular weight materials; and (5) the procedure seems to be unaffected by the type of emulsifier or dispersing agent used.

2. Procedure.

a. Equipment. The concentration of Igetex (buna latex) at Hüls - Bldg.188 - is carried out in two 10 cu.m. vessels. Both vessels are jacketed to permit cooling by refrigerated brine. Special vigorous agitation, or more specifically beating, is obtained by two different types of stirrers used in the two vessels.

The older design stirrer in one vessel consists of 7 sets of 4-armed paddles which are mounted on a vertical shaft running at about 30 RPM, and which pass between 4 groups of horizontal baffles mounted at 90° spacing on the sides of the vessel. More complete details are given in the original report of December 15, 1944, by Dr. Schneider (I/256/Ep). The latest and simplified design used inthe second vessel at Hüls consists of two widefaced anchor type impellers mounted on the vertical shaft at 90° angles to each other and perforated by rectangular openings. Four narrow baffles are mounted vertically along the sides of the vessel to improve turbulence and heat transfer at the vessel wall.

b. Operation. Latex of 25-30% dry rubber content is stirred into foam in the concentrating vessels described above while being cooled to the thickening point. Simultaneously about 0.2-0.5% Na_2Co_3 based on the latex weight is added as a solution in order to raise the "stockpunkt" from 10-12°C to about 15°C. The original latex liquid volume (4-5m^3) increases 3-5 times when it is beaten to foam over a period of 3-8 minutes. The total time of stirring the foam is primarily dependent upon the time required to cool the latex to the "stockpunkt", or preferably a few degrees below. This ordinarily requires 1-1½ hours. After the desired temperature is reached, stirring is continued a short time whereupon the foam begins to agglomerate ("Kornen") into small granules. Stirring is terminated and the foam is allowed to break into two phases during a period of 4-5 hours. The serum which separates is essentially free of rubber while the upper layer is a curdlike concentrate of latex containing 45-52% rubber. The clear serum was reported in one case to contain 75-80% of the original Nekal, 50-60% of the inorganic salts and 18-22% linoleic acid. After serum is drained off the concentrate



Two Types of Latex Concentrating Vessels used at the Hüls Buna Plant.

is heated a few degrees and is then also drained from the bottom of the vessel into steel drums.

Since the thickening point varies with batches and types of latex, addition agents such as Na_2CO_3, soap or "Latekoll" are used for adjusting it to the proper level. It was intimated that latekoll, which was used frequently at Hüls, was a Methacrylate type product. The desired treatment for any batch of latex was determined by laboratory tests and the necessary amount of addition agent was added at the start of the concentration operation. A "stockpunkt" of 12-14°C was considered desirablo. It was stated that the thickening point of latex is lowered noticeably when the emulsifier concentration is decreased by dilution.

Concentrated latex prepared at Hüls was shipped to tire plants in 475 Kg (net weight) galvanised steel drums where it was used for cord dipping and cloth impregnation. Latex was filtered prior to drumming to remove a small amount of pre-coagulum which formed during concentration.

c. Production. It was stated that since July 1944, only Buna S 3 was concentrated at Hüls. However, plant records indicated a production of 72,507 Kg (as 100% rubber) of 45% solid IgetexSand 169,813 Kg. of 45% Igetex SS.

C. Experimental Polymerization Equipment at Hüls

At Hüls, laboratory research polymerizations were conducted in sealed glass test tubes. The portion of the research building in which these reactions were conducted and the records relating to this work were destroyed by bombing, so no specific information was obtainable.

A large pilot-plant (Building 159) was located adjacent to the research building, half of which was used for work on synthetic rubber and resins and the other half of which was devoted to work on miscellaneous chemicals. Pilot-plant polymerizations were started in August, 1942. By far the largest amount of work was done on Buna S type polymers, but when Perbunan production was shifted temporarily to Hüls a small development program was undergone.

Equipment:

Four 12 liter pots made of iron were located in the building, but it was claimed that these were not used because not enough polymer could be produced in them to get the desired physical testing.

Six 36 liter lead-lined iron reactors were used for batch-wise polymerization. These reactors were equipped with large rectangular paddles which rotated at 90 RPM. The packing around the agitator shaft was composed of leather soaked in glycerine. No counter-pressure was used on the packing. It was designed so that a packing nut could be adjusted to put pressure on the stuffing box. The maximum pressure reached in the vessel was stated to be 15 atmospheres, and it claimed that the leather-glycerine packing formed a very good seal. For following the temperature of the contents, each vessel contained one thermometer well and one thermocouple. In charging, an emulsion of styrene and the aqueous phase was sucked into the pots by vacuum. The butadiene then was pressured in. From a batch in one of these 36 liter pots, approximately 12 kg of polymer was produced.

The pilot-plant continuous polymerization unit consisted of six reactors of 150 liters each, mounted in two rows of three reactors each with the whole unit enclosed in a large box with only the reactor heads protruding. The reactors were equipped with the same fittings and agitation as used in the 36 liter pots. For the continuous unit there was one 500 liter make-up tank for aqueous phase and one 1500 liter tank for preblending the monomers. Steam condensate was used as water for all pilot-plant polymerizations. Each of the monomers were weighed out and then run into the blending tank. From the large blend tank the monomers were transferred to two calibrated measuring tanks used alternately. Sight glasses permitted a reading of the amount being charged per hour. Two similar tanks were used for charging the aqueous phase. Four small piston pumps were used for charging diproxid dissolved in styrene.

The latex coming out of the continuous polymerization line was run through a filter and into a 6 cubic mete tile-lined tank where phenyl-beta-naphthylamine was added and where the unreacted monomers were flashed off. When Buna S 3 was made, $FeSO_4$ was added to the stabilized latex to improve the heat softening properties of the polymer. For 5.5 to 6 kg of polymer, 20 grams of $FeSO_4 \cdot 7H_2O$ was added. Coagulation was accomplished in enamel-lined vessels under a hood.

A large experimental fourdrinier and a continous drier were located in the pilot-plant but were not used because they were too large.

An experimental unit for latex concentration was located on the balcony of the pilot-plant. It consisted of a jacketed 55 gal. drum agitated with a beater containing four flat square blades supported on a square frame. The beater rotated at 110 RPM. Cold jacket water at 4°, 6° or 8°C lowered the temperature of the latex and caused it to agglomerate to larger particles and allowed a creaming operation to occur. This procedure has been described in detail in another report.

Also on the balcony of the pilot-plant was a small production unit for manufacturing approximately 20 tons per month of Resin SAX (Styrene-Acetophenone-Xylol) for the lacquer industry.

Information reported herein was obtained from Dr. Schneider, the man in charge of pilot-plant work in the Buna Division at Hüls. Reference to Dr. Schneider's files revealed that pilot-plant polymerizations at Hüls had been confined primarily to problems of production such as substitution of H_2SO_4 for acetic acid in coagulation when the latter became scarce. Actually, very little work of development nature had been conducted.

D. BATCH PRODUCTION OF PERBUNAN

Because of bombing damage to the Leverkusen Perbunan plant in October 1944, some Buna N had to be produced at the Hüls Chemische Werke. About 43 tons were manufactured during December 1944, acrylonitrile being shipped in from Leverkusen. The procedure and recipe are described below.

	Parts by Weight
Butadiene	74
Acrylonitrile	26
Water	200
[1] Nekal (100%)	4
NaOH (100%)	0.024
$K_2S_2O_8$	0.2
Diethylamine	0.025
Diproxid	0.28

(Added in three equal parts at 0%, 25% and 50% conversion)

Polymerization is conducted in a 20 m^3 V_2A reactor, operated with a 16 m^3 charge. Aqueous phase and acrylonitrile are placed in the reactor and butadiene is measured in. For stopping the reaction, a 10% water solution containing approximately 5 Kg of $Na_2S_2O_4$ is added at 80% conversion. The age-resistor, 3% (on dry polymer) phenyl-beta-naphthylamine in a 20% suspension, is placed in the adjacent vessel, and the Perbunan latex is pumped into the tank and agitated.

For butadiene removal, a single-step recovery unit is used. Unreacted acrylonitrile is not recovered. The latex is coagulated and dried by the following procedure:

Approx. 2.4 m^3/hr. of latex (24.6% solids)
4.5 m^3/hr. saturated NaCl solution plus
4.0 m^3/hr. of water
0.1 m^3/hr. NaOH solution plus 4.0 m^3/hr. of water
15. m^3/hr. of water for the washing.

---

[1] Mixture of Nekal BXG (76-78% alcohol soluble) and Nekal BX (62% alcohol soluble) to give an emulsifier of 70% active ingredient.

Drier temperature:

1st zone - 123 - 140°C.

2nd zone - 130°C.

Speed of the fourdrinier - 5.3 m/minute.

Production - approx. 580 Kg/hr.

Band thickness - 1.5 mm.

The product ought to contain 26% acrylonitrile by nitrogen analysis.

TESTING LABORATORY AT HÜLS.

Summary:

At Hüls there were extensive facilities for mixing and testing rubber compounds. They seemed excessive for purely control purposes and as far as we could determine were not used to good advantage for research and development purposes, although a certain amount of evaluation work was done on softeners and blacks. Some of the smaller rubber items used in the chemical plant were manufactured in this plant and an installation was under way to make even the large items. The reason given for this type of production was that deliveries could not be obtained from normal sources.

* * * * * * *

Equipment:

An essentially complete list of equipment is given in Appendix A. Much of this equipment is standard but there are a few items which deserve special comment.

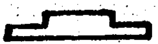
1. The internal mixer and most of the mills could be operated at two speeds.
2. One fifteen inch mill was specially fitted by replacing the normal screw for setting the bite with a hydraulic piston. This permits a slight fluctuation in the opening during milling but maintains constant pressure on the rubber. Dr.Hormuth said that this gave better and more uniform results on mastication tests than do standard mills. This appears to be an excellent idea.

Tests.

According to Dr. Hormuth only one recipe is used for testing all types of Buna although at times they had to vary the softener because of shortages. The same recipe was also used for evaluating the blacks produced at Hüls. A standard procedure of testing was also followed. This procedure is given in Appendix B.

A limited number of standard chemical tests were also used. These are given in Appendix C. For double bond determination the iodine trichloride determination is of doubtful value for synthetic rubber because no provision is made for determining the amount of substitution. The polystyrene test is interesting as a test and also because it indicates the presence of free polystyrane mixed with the Buna.

Extrusion Test. A small tube machine extrusion test was extensively used and all samples were photographed. The die was shaped so that the extruded sample had the following cross section



Tensile and Structure Tests. All tensile tests were run on standard Schopper machines. In the so-called "Structure Test", five nicks are cut on opposite diameters in the inside of Schopper rings by a special device. The specimens are pulled on a Schopper machine using hooks instead of revolving drums. Results are reported as Kg/cm^2. The difference between the tensile strength obtained this way and in the standard Schopper test is considered an indication of structure. It is essentially a tear test.

Temperature Stability Test. In this test a cylinder of standard height is subjected to a constant load for periods of time ranging up to 24 or 48 hours and the time-height curve is drawn. The load is then removed and the curve extended. Thus the first part of the curve is a time-compression curve and the last part, one for time-recovery. The test can be run at a wide range of temperatures both above and below room temperature. From a series of such curves the freezing temperature of the rubber is determined.

Plasticity, was always determined on the Defo machine which has been described in the literature. Six samples are used for each test, three to get approximate weights and three for accurate determination.

General Comments.

The following general comments were made by Dr. Hormuth:

When sulfuric acid was used to replace acetic acid in coagulation, the usual Defo values were obtained but mill breakdown properties were found to be inferior.

At the same Defo value Buna S-3 gave somewhat better extrusions than Buna S, but Buna SR was much better than either of the others.

Buna SR was about 10°C lower in freezing than Buna SS by the stability test.

Buna SS is bad for hysteresis but Buna SR is about the same as Buna S-3.

APPENDIX A

Laboratory Equipment at Hüls

One Werner-Pfleiderer Internal Mixer
Capacity 2-3 Kg., two speed, Banbury type blades, cold water and steam.

Three standard mixing mills (40 cm)
Front speed 20 and 30(?)RPM, friction ratio 1:1.15, steam and cold water.

One mill as above with mill opening controlled by hydraulic pressure.

One 24 inch standard mill.

One 60 inch standard mill.

Three variable speed tube machines, 40 mm., 80 mm., and 120 mm. diameter.
Cold water and steam.

Four 4 deck presses.
Steam heat, pressure to 200 atmospheres, 24 inches square.

One small press.
Screw pressure, electrical heat.

One small internal mixer for cement.

One small disintegrator for Buna sheet for cement making.

Three vessels for thermal breakdown, two 250 liter capacity, and one 550 liter capacity.

One Schopper Tensile tester.

Two Schopper structure testers.

One Temperature Stability Tester.

Three Defo machines.

Geer Ovens.

~~Bierer Bombs.~~

Hot Air Ovens.

Apparatus for belt flex tests.

Apparatus for bending rod flex tests.

Four Schopper detrition machines.

One constant load hysteresis machine.

A Brabender plastograph had been used for a while and then abandoned.

In process of installation were an 84 inch mill, a large calender, and large presses. They had been making packings and gaskets for use ~~in the plant and planned to expand this~~ operation to larger items, probably linings and pipes for corrosion resistance.

APPENDIX B.

Physical Testing Procedure at Hüls

Tests on Raw Buna: (Perbunan, Perbunan Extra, Buna S, Buna SS, Buna S 3, and Buna SR).

Defo determinations (large sheets):

1. Raw, unmilled (200 g).

2. Raw, after milling 300 g. for 15 passes.

3. Raw, after 30 passes through the colder, tighter mill No. 6. (mastication time noted)

Thermal working at 130°C and 3 atmospheres air pressure:

Samples of the final Buna product are heated for 30, 50, 70 and 100 minutes. All others are heated 50 minutes unless otherwise noted.

Small Defo sheets are prepared and dusted lightly with zinc stearate.

Compounding:

Roll temperature 40°C.

			Perbunan (Extra)	Buna S,S3 or SR.	Buna SS.
			5 passes through tight mill,then run in band for 2 minutes	5 passes through tight mill, then run in band for 2 minutes	1 pass through tight mill then run in band for 2 minutes.
Buna	600 g.	100			
Kautschol	30	5			
Stearic acid	12	2	8 min.	5 min.	5 min.
ZnO RS	30	5			
Sulfur	6	1	3 min.	3 min.	3 min.
Black CK3	240	40	15 min.	15 min.	12 min.
	918 g.	153	28 min.	25 min.	22 min.

Stocks are given 2 passes through a tight mill.

For determination of Defo, 152 grams are cut off and sheeted out on the mill to approximately 1 mm.

Vulkacit AZ is then added to the remainder of the stock in the following amounts (2 minutes milling):

Perbunan (Extra)	Buna S, etc.	Buna SS.
3.0 g.	4.0 g.	4.0 g.
.6 PHR	.8 PHR	.8 PHR

The stocks are then given 3 passes through a tight mill and sheeted out to 10 mm. gauge. Finally, the stock is weighed.

Curing:

2 sheets each at 30, 60, and 90 minutes at 2.1 atmospheres (extra sheets cured at 60 minutes).

2 sheets each at 15, 30, and 45 minutes at 1.0 atmosphere.

Extrusion:

A small tread section is extruded.

Physical testing:

1. Defo tests for raw, heat-treated, and pigmented sheets.
2. Tensile, modulus, and hardness at 20°C on the 60 minute cure.
3. Rebound at 20, 70, and 100°C on the 60 minute cure.

APPENDIX C

Chemical Tests used at Hüls

Analyses of Buna S and Buna SS

Determination of the Butadiene Content by Determination of Double Bonds.

After addition of phenyl-beta-naphthylamine and approximately 2 cc. of glacialacetic acid, 30 cc. of latex are coagulated with approximately 1 liter of methanol and the coagulated rubber is dried in vacuum at 50°C.

To 0.4 grams of Buna S or 0.5 grams of Buna SS, 40 cc. of nitrobenzene are added and the mass is allowed to soak overnight. The sample is then boiled in a nitrobenzene bath for 10-15 minutes at 210°C, stirring with a glass rod and it is again cooled to room temperature. 15 cc. of a 1 N iodine trichloride solution are put in and it is allowed to stand two hours in ice.

In a 1 liter flask approximately 20 cc. of a 1 N potassium iodide solution is added. The sample treated with iodine chloride is added along with two rinses with methanol and the flask is filled half full with water.

Nitration with N/10 $Na_2S_2O_3$
Indicator - Starch solution.

Calculation:

cc. 1 N ICl_3 - cc. N/10 thiosulfate · f = % butadiene

f = 0.75 for Buna S, or 0.60 for Buna SS.

Polystyrene Determination.

1 gram of Buna is dissolved in nitrobenzene at 210°C. The solution is cooled in a 1 liter flask, 5 cc. of KOH (30%) and 500 cc. of $KMnO_4$ solution (70 g/1) is added. The solution is shaked for 15 hours. The

remaining permanganate is destroyed with 10% Na_2SO_3 solution, nitrobenzene is steam distilled off. The MnO_2 remaining behind is dissolved in hot water, H_2SO_4 and bisulfite. Free polystyrene is filtered off and dissolved in benzol; this solution is evaporated in a crystallizing dish on a water bath and dried for one hour at 100°C and weighed.

Calculation:

$$\frac{C \cdot 100}{E} = \%\ \text{free polystyrene.}$$

Linoleic Acid and Paraffin Fatty Acid Determination.

15 grams of Buna are extracted in a soxhlet with 350 cc. methanol for 2½ hours. 50 cc. of the extract is shaken twice in a separatory funnel with 100 cc. ether plus 100 cc. water plus 10 cc. 1 $\underline{N}$ NaOH. The aqueous phase is drawn off and titrated against 1 $\underline{N}$ H_2SO_4 (indicator phenolphtalein).

Calculation:

$$\frac{\text{cc } 1\ \underline{N}\ NaOH - \text{cc } 1\ \underline{N}\ H_2SO_4 \cdot F}{E} = \%\ \text{acid}$$

where F for linoleic acid = 27.5
F for paraffin fatty acid = 20.5

Nitrogen Determination.

Phenyl-beta-naphthylamine is determined by Kjeldahl method for nitrogen analysis.

Ash Determination.

1 gram of polymer is ashed over an open flame in a porcelain crucible.

Iron Determination.

5 grams of Buna are ashed. The residue is decomposed with H_2SO_4 - and "Perhydrol". The iron content is determined colorimetrically after the addition of thiocyanate solution.

PART III - APPENDIX.

SUMMARY OF DOCUMENTS - BAGS NO. 2924, 2925, 2926

NUMBER

2924)
2925) - 1 Cost and yield summary, First quarter 1944, for synthetic rubber and intermediate products.
2926)

- 2 Ditto - 2nd quarter, 1944.

- 3 Cost and yield calculations, First quarter, 1944.

- 4 Ditto - 2nd quarter, 1944.

- 5 Ditto - 3rd quarter, 1944.

- 6 Reports on Perbunan, Hard Rubber Lining, and Styrene Stripping.

- 7 Reports from June 1944 meeting of Process Control Group in Oppau.

- 8 Research Report. Fractionation of Buna S and SS.

- 9 Research Report from Ludwigshafen, August 1942 - Emulsion Polymerization.

- 10 Research Report from Schkopau, October 1939 - "Effect of throughput on Buna S polymerization".

- 11 File from Dr. Baumann on Misc. Catalyst manufacture.

- 12 Research Memoranda from Organic Division.

- 13 Research on hydrogenation of aldol at 300 and 700 atm.

- 14 Butadiene production and research records.

- 15 General research report on acetylene - July, 1937.

- 16 Monthly reports on styrene plant No. 1.

- 17 Ethylene production from alcohol.

- 18 Acetylene hydrogenation.

- 19 Utilization of higher acetylenes.

2924)
2925) - 20 Research on acetylene arc.
2926)

- 21 Rubber coating.
- 22 Memoranda from Organic Division - catalysts.
- 23 Butol distillation.
- 24 Monthly reports on styrene No. 2.
- 25 Ethylbenzene production.
- 26 Lebedev butadiene process research.
- 27 Aldol manufacture.
- 28 Acetylene arc plant records.
- 29 Research on butol manufacture.
- 30 Acetaldehyde catalyst.
- 31 Acetaldehyde - general memos.
- 32 Ethylbenzene plant reports.
- 33 Benzol plant reports.
- 34 Acetylene purification and concentration plant reports.
- 35 Buna S plant reports.
- 36 Correspondence with Continental.
- 37 Acetaldehyde production plant reports.
- 38 Buna correspondence.
- 39 Polymerization literature.
- 40 Aldol tests.
- 41 Buna plant reports.
- 42 Rectifier of arc acetylene plant reports.
- 43 Ethylene recovery from coke oven gas.

~~2924)~~
2925) - 44 Aldol hydrogenation No. 2.
2926)

- 45 Aldol memoranda.

- 46 Aldol hydrogenation No. 1.

- 47 Polystyrene plant reports.

- 48 A. P. Harz (Plastic) plant reports.

- 49 Perbunan plant reports.

- 50 Buna plant reports.

- 51 Polymerization plant reports.

- 52 Acetaldehyde distillation.

- 53 Production and Cost Statistics 1940-1945.

- 54 Production and cost summaries 1944.

- 55 Latex concentration.

- 56 Buna production data.

- 57 Patent file - catalytic reactions.

- 58 Patent file - synthetic rubber.

- 59 Hüls maps.

- 60 Buna experiments.

- 61 Activation of buna polymerization.

- 62 Internal reports on buna.

- 63 Polymerization experimental data.

- 64 Quarterly summaries of plant operations.

- 65 Patent file - emulsion polymerization.

- 66 Distyrene manufacture.

- 67 General development reports.

2924)
2925) - 68 Distyrene manufacture.
2926)

- 69 Miscellaneous buna tests.
- 70 Patent file - emulsionpolymerization.
- 71 Building and personnel information.
- 72 Koksagiz experiments.
- 73 Quarterly summaries of all departments.
- 74 General file on buna.
- 75 Miscellaneous blueprints on buna plant.
- 76 General memos on buna.
- 77 Crotonaldehyde condensation.
- 78 Buna testing.
- 79 Photographs of plant.
- 80 File from Organic Division.
- 81 Misc. file from Dr. Bauman's office.
- 82 Linde process description.
- 83 Letter file.
- 84 Miscellaneous reports.
- 85 Rubber testing equipment.
- 86 Reports on Buna testing equipment.
- 87 File of correspondence with other I.G. plants.
- 88 Miscellaneous reports.
- 89 Test results from Leverkusen.
- 90 Analytical laboratory tests.
- 91 Rubber evaluation test reports.

2924)
2925) - 92 Evaluation of new products.
2926)

- 93 Rubber evaluation test reports.

- 94 Compounding tests.

- 95 Evaluation laboratory data.

- 96 Test data on buna.

- 97 Buna compounding test formulas from Leverkusen.

- 98 Reports on rubber testing.

- 99 Research reports from Leverkusen.

- 100 Rubber test recipes and procedures.

- 101 Evaluation reports of rubber and compounding materials.

- 102 Test data on carbon black.

- 103 Misc. tests on buna.

- 104 Process flow sheets and descriptions.

SUMMARY OF BOMB DAMAGE.

1. Acetylene Plant - Damaged by June 22/43 raid. Gas holder exploded. All main damage now repaired.

2. Styrene Plant - 1 reactor demaged. 2 pure styrene stills badly damaged.

3. Ethylbenzene Plant 1 distillation train badly damaged.

4. Buna Plant - 1 finishing building badly damaged.

5. Catalyst Manufacture Building - Destroyed.

6. Research Building Center destroyed.

7. ~~Gas supply - Gas from Gelsenkirchen and Scholven~~ cut off due to bombing of these plants. This had most important effect on plant operations.

8. Benzol Plant - 1 distillation train slightly damaged.

9. Chlorine Plant - Signification and Storage badly damaged.

10. Buna Storage - Top floor bombed and destroyed by fire.

11. Piping. - Miscelleneous steam and chemical header lines destroyed by bombs.

12. Cooling tower - One badly damaged.

PRODUCTION IN METRIC TONS.

Date.	Butadiene	Styrene	Buna S	Buna SS	Buna SR	Buna S3	Latex S	Latex SS	Total Buna.
1940									
Jan.									
Feb.									
Mar.									
April.									
May.									
June.									
July.									
Aug.	143			212					212
Sept.	-	74		345					345
Oct.	209	125	180	-					180
Nov.	399	276	175	347					522
Dec.	457	244	-	967					967
Total	1208	644	355	1870					2045
1941									
Jan.	507	461	70	721					791
Feb.	784	315	589	316					706
Mar.	729	545	601	721					1323
April.	1290	749	582	1168					1749
May.	1417	930	720	1423					2141
June.	1016	521	642	735					1377
July.	1454	683	933	741					1674
Aug.	1723	975	1230	1180					2409
Sept.	1793	1151	1472	1271					2744
Oct.	2531	1295	1871	1355					3226
Nov.	2530	1230	2093	1438					3531
Dec.	2326	1224	1815	1334					3149
Total	18100	10082	12619	12401					25020

PRODUCTION IN METRIC TONS (Continued)

Date.	Butadiene	Styrene	Buna S	Buna SS	Buna SR	Buna S3	Latex S	Latex SS	Total Buna.
1942.									
Jan.	623	302	222	752	41			-	1015
Feb.	1892	1078	815	1315	509			1	2641
Mar.	2649	1502	1912	1321	248			1	3482
April.	2278	1523	1197	1435	373			2	3007
May.	2317	1269	967	1616	238			4	2855
June.	2231	1313	1094	1536	442			8	3080
July.	2632	1400	1488	1329	480			9	3307
Aug.	2619	1446	1436	1207	576			16	3235
Sept.	2654	1578	1774	1112	470			8	3364
Oct.	2903	1658	1706	1230	584			4	3524
Nov.	2816	1738	1777	1198	612			10	3597
Dec.	2984		1614	1362	583			14	3574
	28596	16474	16030	15415	5158			77	36680
1943									
Jan.	2942	1480	1947	1364	612		-	19	3942
Feb.	2625	1498	1460	1235	835		20	7	3557
Mar.	3148	1703	1500	1313	993		1	21	3828
April.	2907	1532	1497	1332	952		-	14	3795
May.	2944	1616	1723	1336	897		-	-	3956
June.	1966	1052	1285	983	221		9	-	2498
July.	-	-	20	4	1		8	-	33
Aug.	656	613	184	960	43		11	-	1197
Sept.	1255	906	300	1115	10		1	13	1438
Oct.	2639	1269	1402	1250	238		17	4	2910
Nov.	2726	1463	1701	1307	563		10	11	3593
Dec.	2954	1583	2088	1206	411		20	18	3744
	26782	14714	15109	13404	5777		97	107	34693

PRODUCTION IN METRIC TONS.

Date.	Butadiene	Styrene	Buna S	Buna SS	Buna SR	Buna S3	Latex S	Latex SS	Total Buna.
1944									
Jan.	3124	1572	1664	1587	611	-	7	20	3889
Feb.	2916	1734	1983	1939	13	-	15	10	3960
Mar.	3257	1783	2094	1266	695	-	-	24	4079
April	2826	1590	2125	1113	40	-	-	20	3660
May.	2419	1214	1820	1095	24	11	2	18	2970
June	2787	1365	921	1108	1017	224	19	2	3291
July	2559	1428	1399	1242	-	493	-	20	3153
Aug.	2691	1355	1055	1270	302	609	-	12	3247
Sept	2738	1171	1800	1142	-	621	-	23	3587
Oct.	2734	1267	1345	1201	-	996	18	7	3568
Nov.	1459	903	410	354	153	1338	11	10	2276
Dec.	1409	609	-	-	202	1210	-	4	1415
	30918	15993	16616	13317	3418	5502	72	180	39105

December 1944 made 43 tons of Perbunan.

SUMMARY OF COSTS - HÜLS.*

RM/100 kg.

		Ethyl-ene	Acetyl-ene	Ethyl-benzene	Styrene	Acetal-dehyde	80% Aldol	Butol	Buta-diene	Buna S	Buna SS	Buna SR
1940	III				322				243			
	IV	142	76	56	218	97	76	144	366			
1941	I	228	71	114	170	73	53	91	229			
	II	116	60	83	139	57	49	77	184			
	III	90	48	66	111	48	42	66	155			
	IV	59	36	55	82	37	34	52	123			
1942	I	70	51	61	96	49	42	67	157			
	II	84	46	66	100	42	38	62	150	186.94	192.29	191.51
	III	84	54	67	100	45	40	65	154	194.23	202.96	200.63
	IV	81	50	56	80	40	39	64	150	169.60	174.16	174.18
1943	I	64	45	50	77	36	35	54	127	157.50	161.55	161.67
	II	67	45	53	79	38	38	59	137	156.58	160.42	168.28
	III	223		120	176	-	110	122	439	603.80	547.50	530.04
	IV	91	60	66	104	47	47	75	130	205.51	209.18	215.44
1944	I	55	40	52	76	32	32	48	115	141.03	146.46	148.28
	II	73.39	50.19	54.34	84.72	40.95	38.62	60.76	142.13	174.25	169.90	170.56
	III	92.27	65.79	68.18	100.52	51.58	47.81	73.00	169.22	205.04	198.33	206.83
	IV											

* Numbers without decimals estimated from chart in Doc.2925 - 53.

SUMMARY OF YIELD 1944 (100 kg output)

BUTADIENE PROCESS.

		Input.	Output.		Yield % of theory
I. Acetaldehyde Manufacture.	Acetylene	64.48	Acetaldehyde	100.00	91.7%
	Nitric acid	1.52	Recycle acetylene.	0.11	
	Iron sulfate	0.80	Acetone	trace	
	96% H_2SO_4	0.65			
	NaOH	1.00			
	Mercury	.01			
II. Aldol Manufacture	Acetaldehyde	82.75	Aldol (80%)	100.00	99.1
	KOH (100%)	0.13	Potassium phosphate	0.15	
	H_3PO_4 (as P_2O_5)	0.12	Sodium phosphate.	0.003	
	NaOH (100%)	0.01			
III. 1,3 Butylene Glycol manufacture.	Aldol (80%)	98.83	Crude butol	100.00	98.9
	Hydrogen (m^3)	26.99	Hydrogen (m^3)	.35	
	BBE catalyst	0.05			
IV. 1,3 Butylene Glycol distillation.	Crude butol	146.00	1,3 butylene glycol	100.00	81.9
			Butanol (100%)	5.56	
			Sec.butanol	0.20	
			Ethanol (100%)	7.29	
			Hexanol.	0.39	
			Toppings.	0.01	
			Residue	3.78	

SUMMARY OF YIELD 1944 (100 kg output) Ctd..

BUTADIENE PROCESS.

V. Butadiene Manufacture.	Input	Output			Yield % of theory
Pure butol	206.68	Butadiene		100.00	80.6
Catalyst	13.28	Butadiene Oil	V	5.34	
		"	Z	0.04	
		"	A	1.06	
		Prolin		1.61	
		Carboresin	H	1.56	
		Butyraldehyde		1.18	
		Propylene		1.54	
		Fraction I		2.91	
		Fraction II		0.89	
		Fraction B		0.36	
		Oil		0.49	
		Fraction III		trace	

STYRENE PROCESS.

I. Ethylbenzene Manufacture.	Input	Output		Yield % of theory
Benzol	77.75	Ethylbenzene	100.00	94.5
Ethylene	28.10	Residue	0.42	
Al Cl_3	2.57	Plasticator RA	3.62	

II Styrene Manufacture.

Ethylbenzene	112.97	Styrene	100.00	90.2
Catalyst		Benzol-tolnol	3.66	
Hydroquinone	0.01	Residue	1.60	

GERMAN PLANNED PRODUCTION OF SYNTHETIC RUBBER

SEPTEMBER 1941* (Thousands of metric tons)

	1941		1942				
Quarter	IV	Total	I	II	III	IV	Total
Schkopau.							
Buna S	11.2	39.8	13.5	15.0	15.0	15.0	58.5
Buna SS	-	-	-	-	-	-	-
Numbered Bunas	0.5	1.9	0.6	0.6	0.6	0.6	2.4
Hüls.							
Buna S	6.2	13.05	3.0	3.2	3.7	4.05	13.95
Buna SS	3.7	12.0	6.0	6.0	6.6	7.6	26.2
Ludwigshafen							
Buna S	-	-	-	-	1.3	6.4	7.7
Auschwitz							
Buna S	-	-	-	-	-	-	-
Leverkusen							
Buna SS	0.48	0.48	0.27	0.27	0.27	0.27	1.08
Buna N	0.6	2.5	0.8	1.1	1.1	1.1	4.1
Total Buna SS	4.18	12.48	6.27	6.27	6.87	7.87	27.28
Total Buna S	17.4	52.85	16.5	18.2	20.0	25.45	80.15
Total numbered Bunas	0.5	1.9	0.6	0.6	0.6	0.6	2.4
Total Buna N	0.6	2.5	0.8	1.1	1.1	1.1	4.1
GRAND TOTAL...	22.68	69.72	24.17	26.17	28.57	35.02	113.93

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* Source - Buna Vortrag Dr Ambros 6/11/41 Target 30/4.17

GERMAN PLANNED PRODUCTION OF SYNTHETIC RUBBER. Contd....

	1943					1944				
Quarter	I	II	III	IV	Total	I	II	III	IV	Total
Schkopau										
Buna S	15.0	15.0	15.0	15.0	60.0	15.0	15.0	15.0	15.0	60.0
Buna SS	-	-	-	-	-	-	-	-	-	-
Numbered Bunas	0.9	0.9	0.9	0.9	3.6	0.9	0.9	0.9	0.9	3.6
Hüls										
Buna S	3.45	3.5	3.5	3.5	13.95	3.5	3.5	3.5	3.5	14.0
Buna SS	9.0	9.0	9.0	9.0	36.0	9.0	9.0	9.0	9.0	36.0
Ludwigshafen										
Buna S	7.5	7.5	7.5	7.5	30.0	7.5	7.5	7.5	7.5	30.0
Auschwitz										
Buna S	-	-	1.2	3.0	4.2	4.8	6.7	9.0	12.5	33.0
Leverkusen										
Buna SS	0.3	0.45	0.45	0.45	1.65	0.45	0.45	0.45	0.45	1.80
Buna N	1.2	1.35	1.35	1.35	5.25	1.35	1.35	1.35	1.35	5.40
Total Buna SS	9.3	9.45	9.45	9.45	37.65	9.45	9.45	9.45	9.45	37.80
Total Buna S	35.95	26.00	27.0	29.0	108.15	30.8	32.7	35.0	38.5	137.0
Total Numbered Bunas.......	0.9	0.9	0.9	0.9	3.6	0.9	0.9	0.9	0.9	3.6
Total Buna N	1.2	1.35	1.35	1.35	5.25	1.35	1.35	1.35	1.35	5.40
GRAND TOTAL	37.35	37.70	38.90	40.70	154.65	42.50	44.40	46.70	50.20	183.80

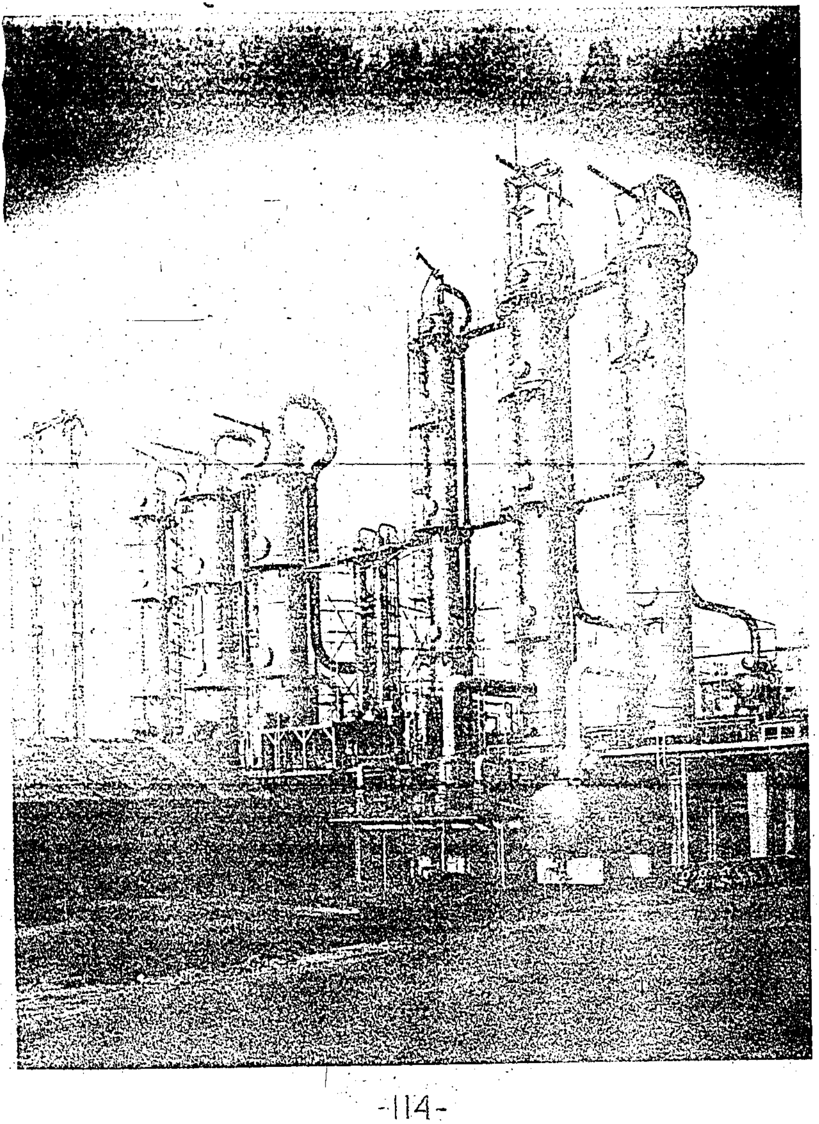
TOTAL RUBBER PRODUCTION IN GERMANY (Metric tons)

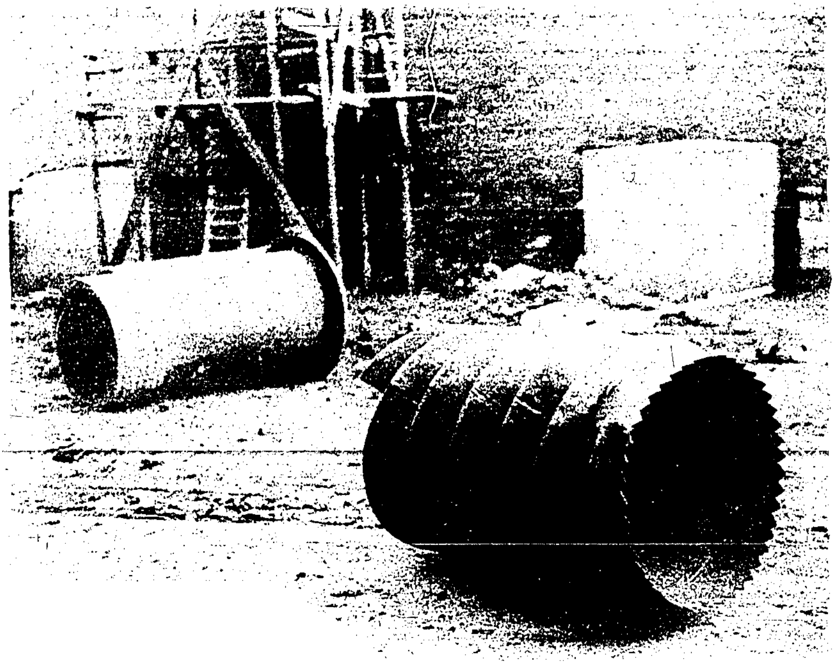
	1937	1938	1939	1940	1941	1942	1943	1944
Buna S types								
Schkopau	2110	3994	20173	34899	40705	57313	67703	45113
Hüls	-	-	-	2045	25020	36680	34693	39105
Ludwigshafen	-	-	-	-	-	-	7181	11955
Leverkusen	***	***	403	193	164	173	992	1320*
TOTAL BUNA S	2110	3994	20576	37137	65889	94166	110569	97493
Buna N								
Leverkusen	** 400	** 640	1126	1898	2631	2824	3656	3129*
Hüls	-	-	-	-	-	-	-	43
TOTAL BUNA N	400	640	1126	1898	2631	2824	3656	3172
Numbered Bunas								
Schkopau	637	848	649	1431	1955	2721	3388	2590
GRAND TOTAL SYNTHETICS	3147	5482	22351	40466	70475	98711	117613	103255

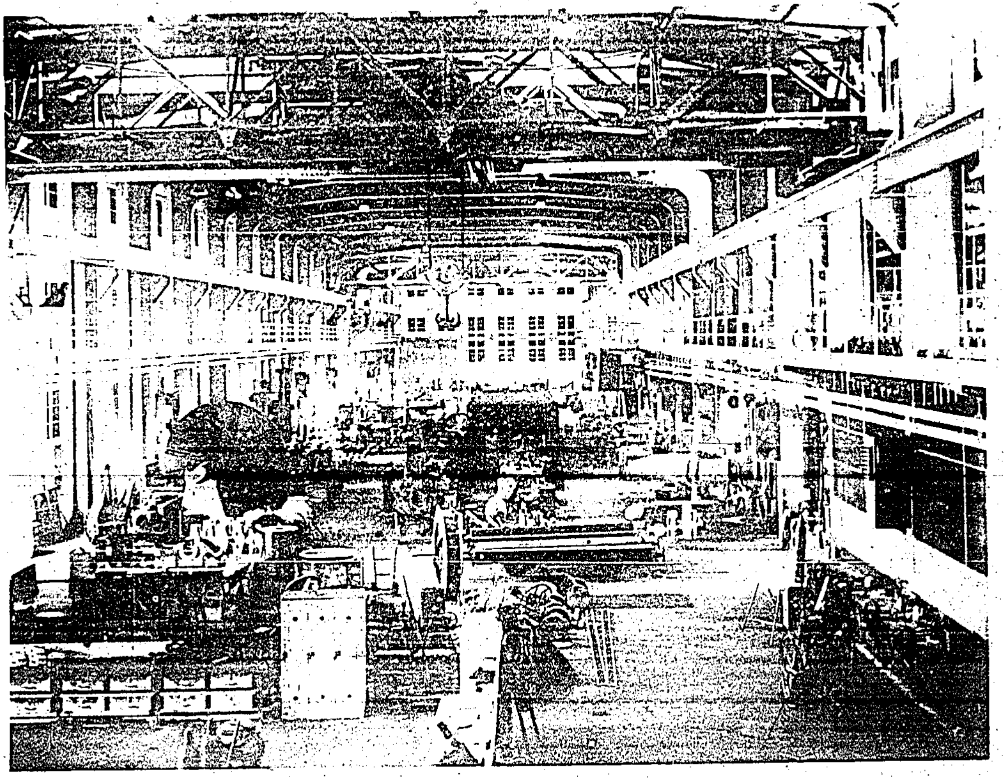
* To Oct 26/44

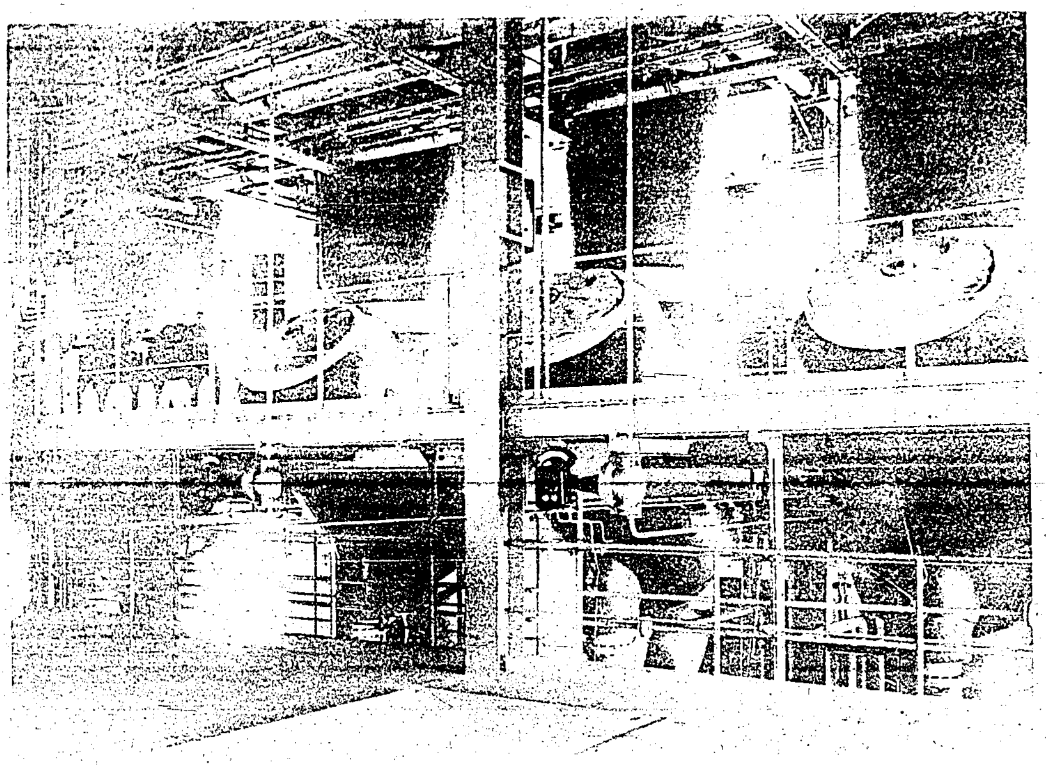
** Approximate.

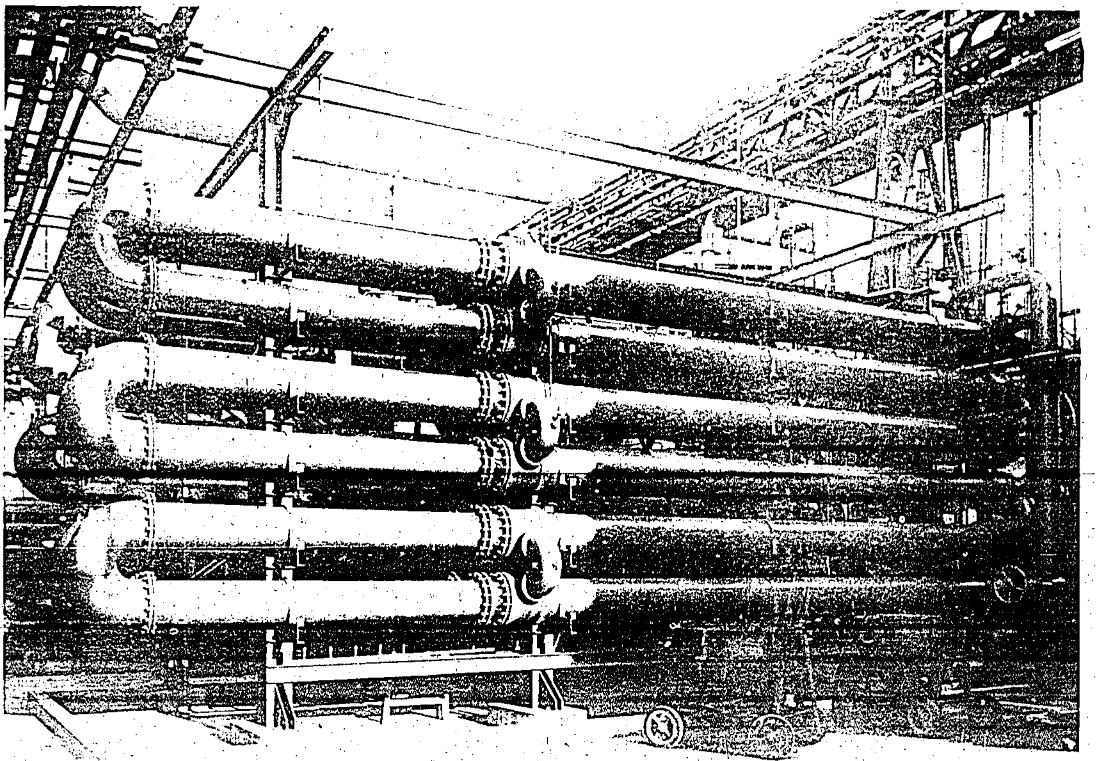
*** Not available.











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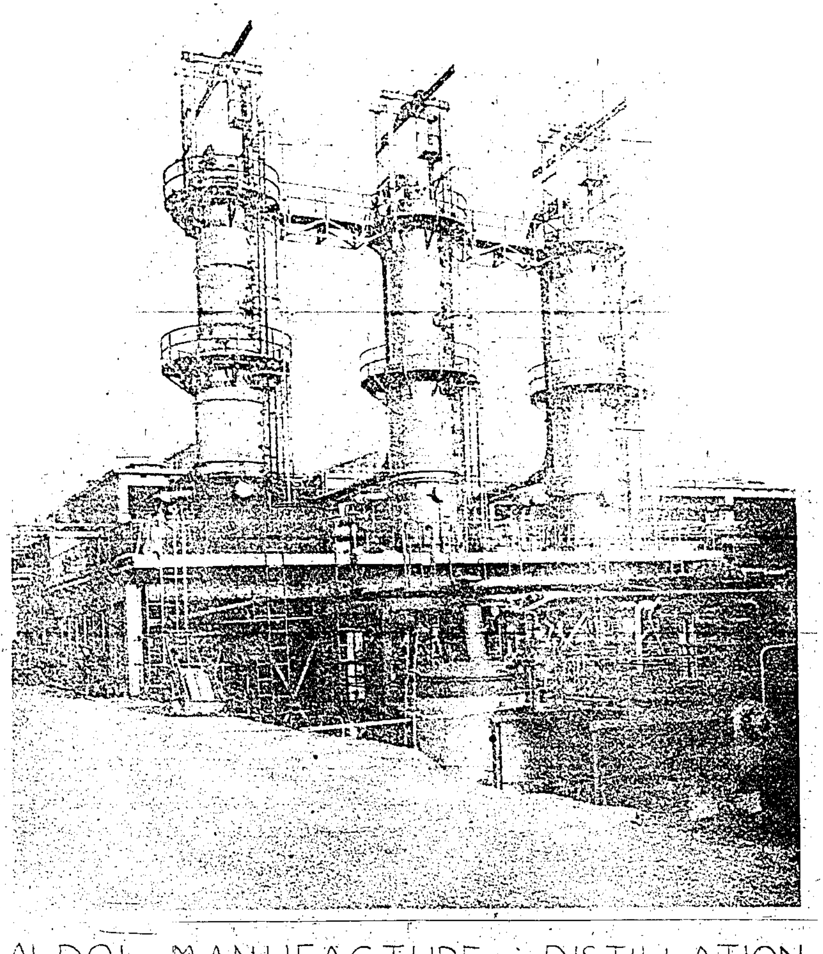

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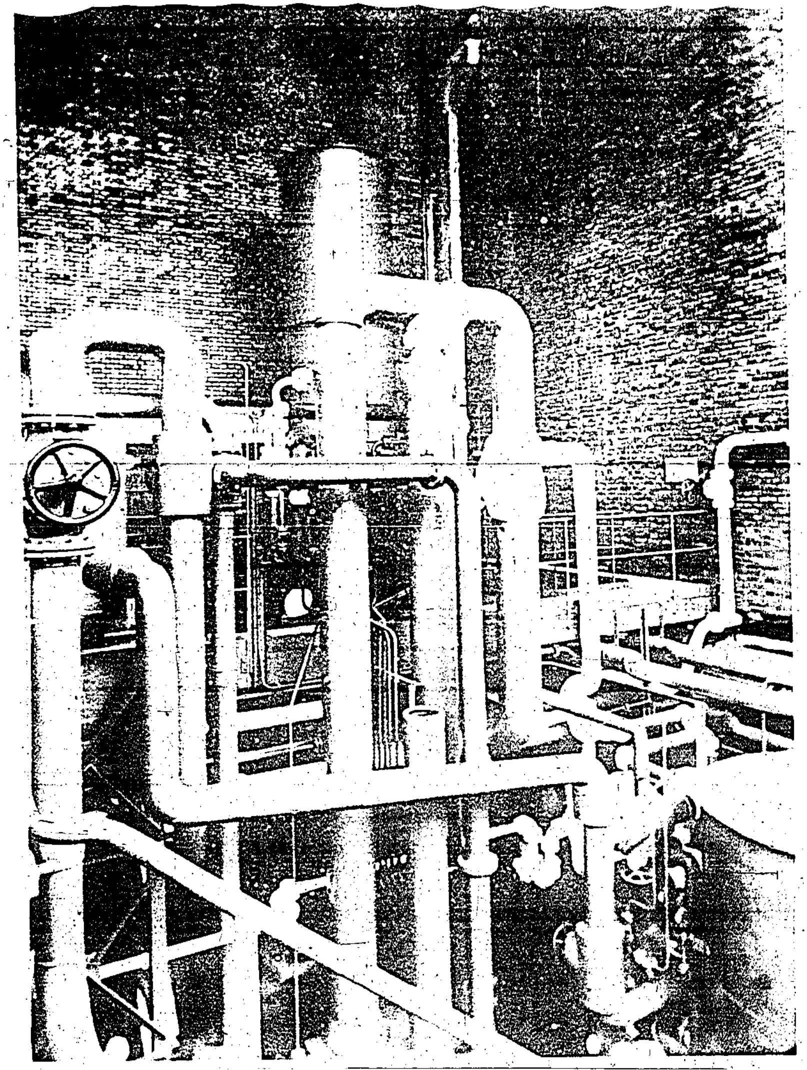

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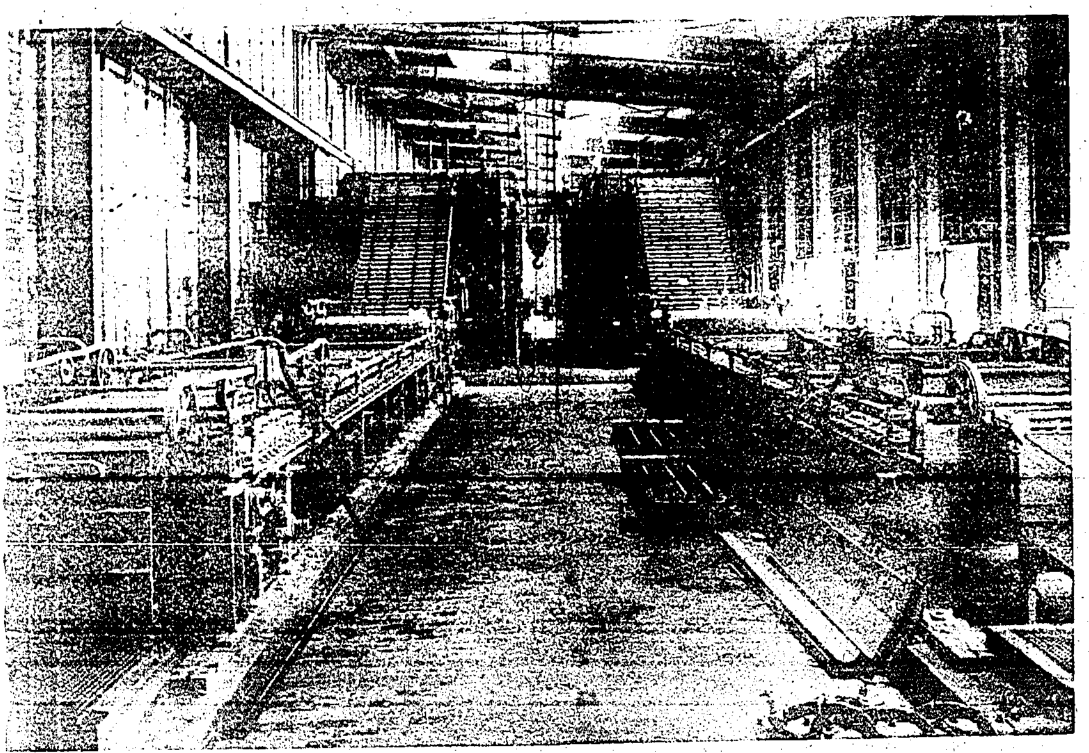
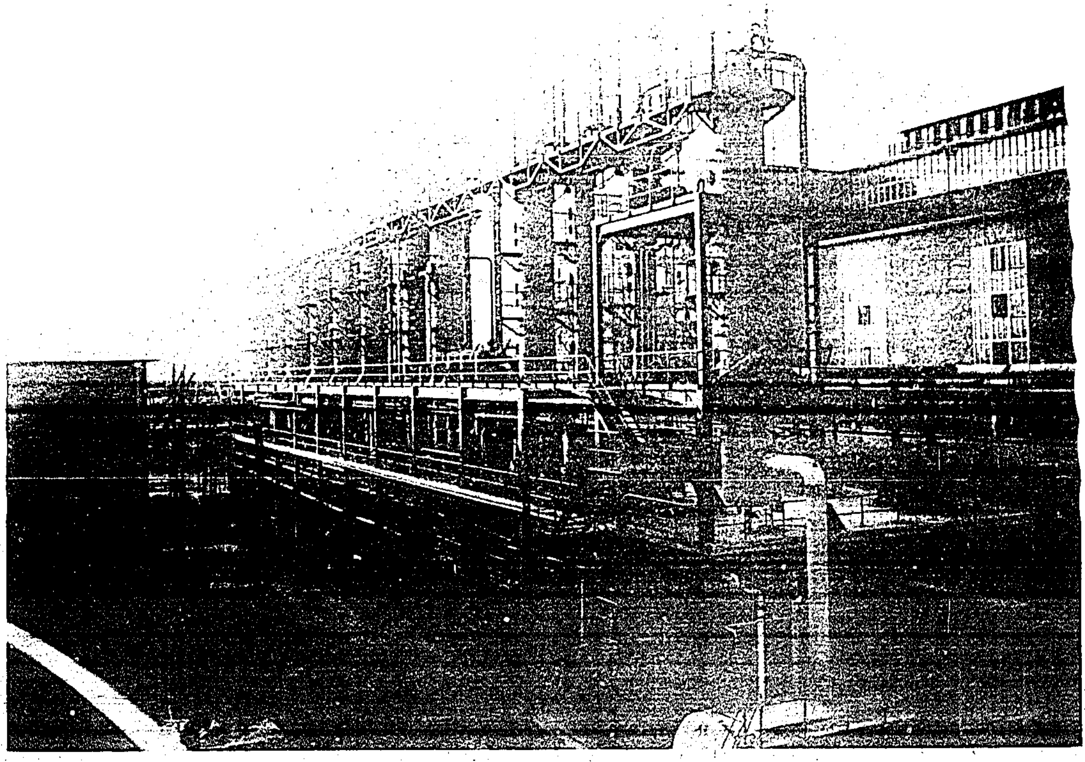


BUNA S FOURDRINIER MACHINES AND DRIERS



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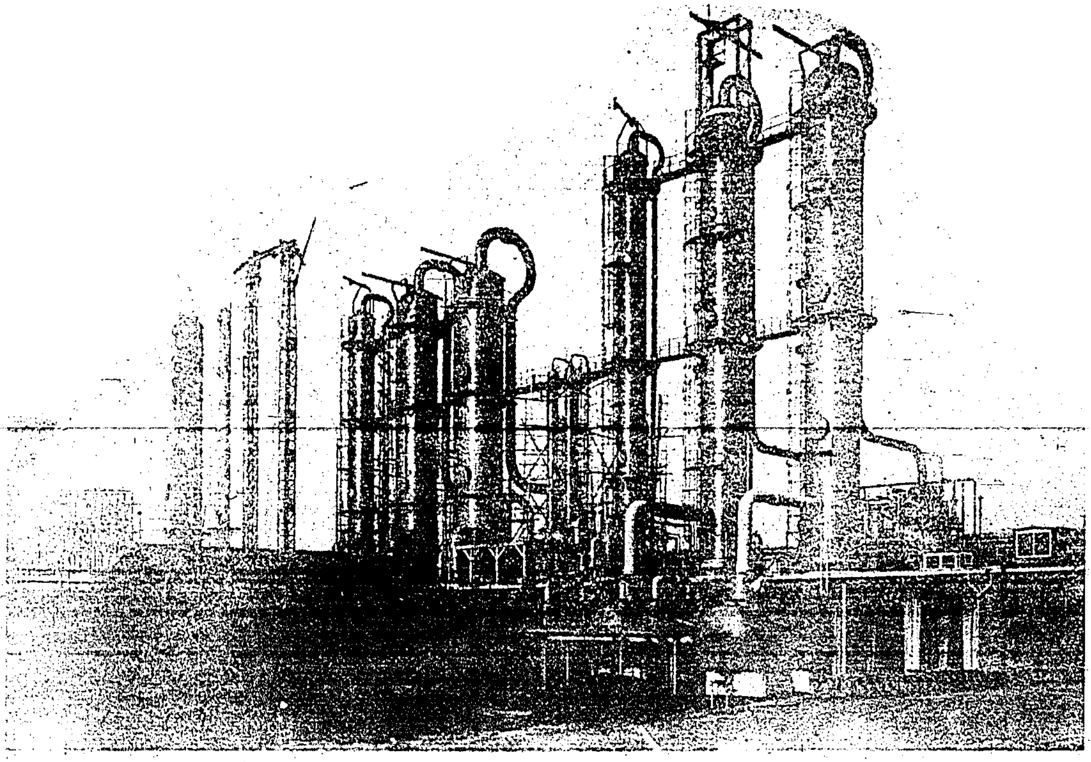

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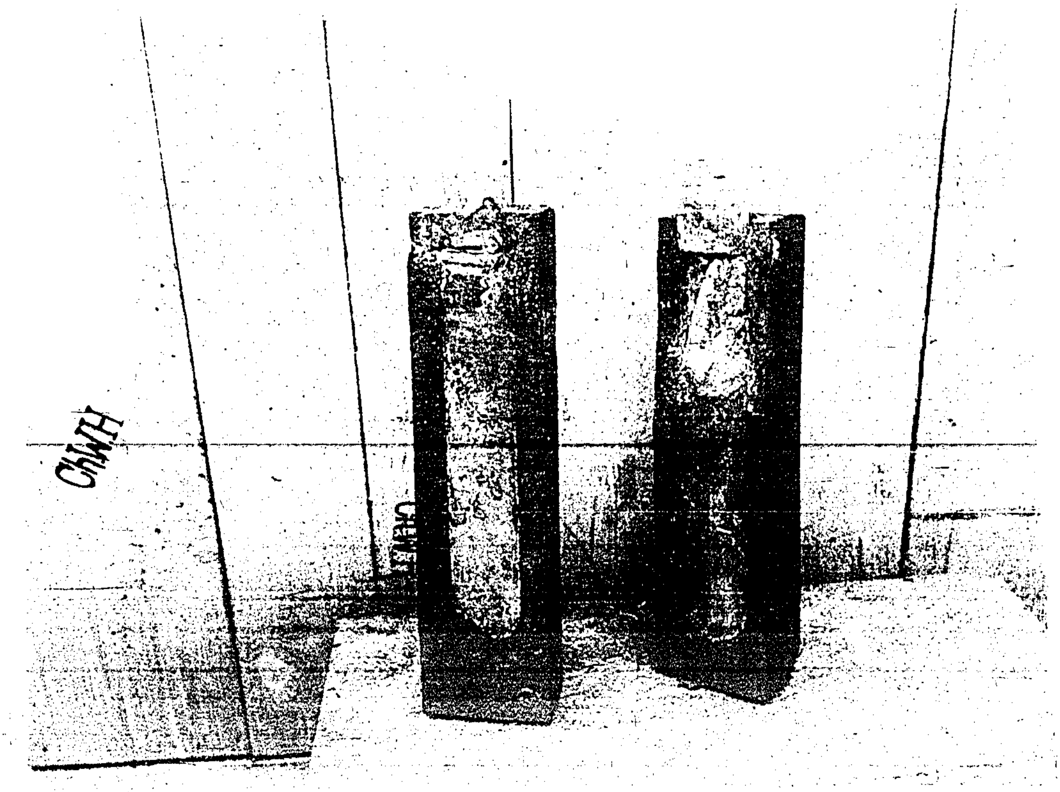
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