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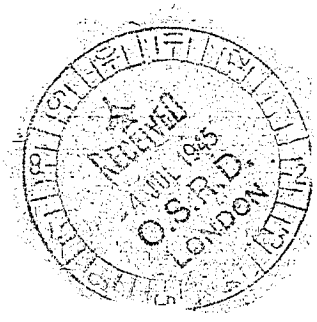
I.G. FARBENINDUSTRIE
SYNTHETIC RUBBER PLANT
LUDWIGSHAFEN

Hopkinson 1.1.



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COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

[redacted]

I.G. FARBENINDUSTRIE SYNTHETIC RUBBER PLANT LUDWIGSHAFEN

MARCH 21 - 30, 1945.

Reported by

RUSSELL HOPKINSON, U.S. LEADER
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Lt. Col. P. D. PATTERSON, Br.
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~~ERNEST T. HANDLEY, U.S.~~
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CIOS Black List Item - 22
Miscellaneous Chemicals.

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear) APO 413

[redacted]

52 p. Illus.

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1. The Ludwigshafen plant had a rated capacity of 30,000 tons per year of Buna S-3 rubber, but this was never attained. Production in 1944 was limited to 12,000 tons due to destruction of gas supply lines, interruption of raw material supplies and damage to installations for the manufacture of butadiene and styrene. Damage to most parts of the plant was extensive.

2. Butadiene was produced at Ludwigshafen by a new synthesis starting from formaldehyde and acetylene rather than from acetylene only as at Huls, Schkopau and Auschwitz. Total coal requirements are 17 tons per ton Buna S.

3. Styrene was produced by continuous alkylation of benzene and ethylene to ethylbenzene, followed by catalytic dehydrogenation of ethylbenzene.

4. Buna S-3 was made by reacting butadiene and styrene in a continuous reactor system and finishing on a paper machine.

5. The total German Buna S capacity was planned for 170,000 tons per year, but production never exceeded 112,000 tons.

6. Koresin, a tackifier for synthetic rubber, is produced from acetylene and isobutyl phenol.

7. Cords for aircraft tires are made from Igamid BS, a nylon-like polyamide obtained from amino-caproic acid.

8. Considerable information relating to the above processes, production data and costs are covered in the main report.

9. Although the plant has been badly damaged and idle since Dec. 15, 1944, it could be reconditioned promptly to produce at half capacity by bringing in styrene from another source. Production costs, however, are higher than the other plants.

10. No information on rubber goods manufacture and very little data indicating research on new rubbers were found.

OPERATIONAL DETAILS OF VISIT TO TARGET

At 6 p.m. March 21, 1945 the following men of the C.I.O.S. Field Team for Miscellaneous Chemicals which was selected by the Working Committee for Section 22 Black List Targets received orders to leave for Ludwigshafen. ✖

Russell Hopkinson, U.S.A., T.I.I.C. Leader.
Lt. Col. H.J.Phelps, Br., M.E.W.
C.C.Monrad, U.S.A., T.I.I.C.
E.W.Glen, U.S.A., Ordnance.
Major D.W.Scott, U.S.A., C.W.S.
J.M.Harris, Jr., U.S.A., C.W.S.
Lt. Col. P.D.Patterson, Br., M.E.W.
Lt. Col. W.G.Davey, Br., M.o.S.
S/Ldr. A.C.Gruneberg, Br., M.A.P.

These men reported with the other field teams assigned to these targets at the C.I.O.S. Secretariat London, at 9.30 a.m. March 22, and departed by bus for Biggin Hill airport. Thence they proceeded by air to SHAEF Main, France, and left the next morning March 23, at 8.15 in a convoy of seven lorries with trailers.

Because of numerous delays and bad road conditions especially as the front line was approached, their destination, T Force Headquarters for the 6th Army at Frankenthal, was not reached until 9.45 a.m. March 25. After billets and passes had been arranged they proceeded to the I.G. plant at Ludwigshafen 7 miles away. The rest of the day was spent in a preliminary survey to determine the physical condition of the plant.

For this purpose the plant area including approximately 860 buildings was divided into eight sections and a team assigned to each. The field team for section 22 was assigned to section 4, an area extending the full depth of the plant east and west and lying north of Buna Strasse as far as and including the power house, carbide plant and acetylene generators. This area was believed to and actually did include most of the buildings involved in the manufacture of synthetic rubber and plastics.

We were told that fighting had ceased in Ludwigshafen at only 5 p.m. of the previous day and that snipers were still being rounded up. Examinations of buildings along the river bank were made within a few hundred yards of the enemy who were occupying the east bank at Mannheim. Furthermore, an artillery barrage of Mannheim from batteries located well behind us was in progress during this and subsequent days.

✖ E.T.Handley joined the team at Ludwigshafen March 26.

The first impression of the section assigned to this team was one of complete wreckage and destruction. Of the hundred and thirty odd buildings in this area hardly one was left intact. Most had collapsed in large sections with steel beams twisted by intense heat and reaction vessels, distillation columns and piping burst, torn from their bases and resting in precarious positions and at all angles.

The rail lines and overhead feeder pipe lines were likewise uprooted, twisted and festooned over the roadways. Large shell craters blocked many of the factory streets. Others were impassable because of overturned and exploded locomotives and tank cars.

Most of this destruction was old, probably from air raids conducted in the third quarter of 1944. Production records verify this conclusion.

On subsequent days a closer examination of the damage was made which indicated that part of the rubber plant at least could, with reasonable expense, be put into operable condition. Details of this estimate appear under Bomb Damage.

A number of Russian workmen were encountered who expressed their pleasure at release from forced labor and the prospects of returning home. Later detailed information was secured which gave the number of "foreigners", Russians, Italians, Czechs, Galicians employed in the rubber plant, indicating that the Germans were outnumbered. Details are given under Personnel.

The next day, March 26, was devoted to interviewing the key operating personnel who had remained at the plant and sorting the documents found in the offices into fields of interest for examination by the proper Field Teams.

The following Executives of particular interest to the Miscellaneous Chemicals Group were all interviewed:

Dr. Georg Niemann.	Director of Diol Division (covering all manufacturing processes from carbide to Buna S).
Dr. Teupel.	Assistant to Dr. Niemann in charge of Polymerization and Finishing.
Dr. Wolfgang Bulow.	Director of Solvents and Plastics Div.
Dr. Ernst Keyssner.	Assistant to Dr. Bulow in charge of Koresin manufacture.

Dr. Hops. Assistant to Dr. Bulow in charge of Polyethylene and Polyamide manufacture.

Dr. Karl Pflaumer. Director of Intermediates Division.

In addition we wished to interview Dr. Ohlinger, an assistant to Dr. Bulow who was in charge of Styrene manufacture, for more detailed information, particularly as to catalyst, but he was not in Ludwigshafen during our stay. He is however, in territory occupied by the Allies and was expected shortly.

The first person interviewed was Dr. Niemann, the least co-operative of the group. Considerable credit is due our interrogator, Major Tilley of the British Army, for his finesse in handling the interviews as a result of which a large number of buried documents giving details of the process were recovered. These proved our best source of information and in general corroborated the verbal information received.

The rest of the plant managers gave full information freely when questioned, frequently volunteering additional data of a helpful character.

After interrogating each manager in the main office and receiving the information obtained, two or more members of the team would accompany the manager to the plant and go over the process step by step filling in any previously omitted details.

On March 27 and 28 the team was divided in to special groups to go over that part of the process for which each was best equipped. Mr. Harris and Major Scott visited target 22/84, the Raschig coal tar plant at Oppau and made a report thereon.

On the evening of March 28, we were told that the large number of investigators were putting a strain on the resources of the T Force, so feeling that we had acquired considerable information of value and had only a few more details to acquire, we arranged to leave the following day.

Messrs. Glen and Patterson, S/Ldr. Gruneberg, Major Dick and Lt. Cols. Phelps and Davy returned to base separately on the 27th.

Messrs. Hopkinson, Handley, Monrad and Harris left by truck at 8.30 on the 28th. Major Scott remained until the 29th.

Mr. Hopkinson and group reached SHAEF Main at 8.30 p.m. the same day and returned by train and boat, reaching London at 6.30 p.m. March 30.

Due to tactical operations by combat troops we were unable to make an investigation of the polyisobutylene plant.

Dr. Ambros, the head of the synthetic rubber development and production in Germany, had fled before our arrival.

A large number of documents were removed as per the list in the appendix. These were studied and the most important microfilmed so that a copy would be available in the U.S.A. Microfilms were sent to the T.I.I.C. Secretariat, Munitions Buildings, Washington, D.C. The documents were returned to M.I.R.S.

A number of documents related to operations at Schkopau. These will be discussed in the report covering the latter plant.

Capacity vs Production

This plant for the manufacture of Buna rubber was begun in January 1941. It was designed to have a capacity of 30,000 tons per year, which rate it never achieved. Its highest output was 2,000 per month which it reached only in March 1944.

A study of the construction progress reports shows that the Polymerization and Finishing plants were substantially ready for production around January 1, 1943.

The production records available started as of March 1, 1943, and showed no finished production until March 23. The attached sheet shows the production record from this date onward. Other records indicate that there was a pilot plant in operation prior to this time which was capable of making 20,000 Kg per month.

It is worth noting that 15 days production was lost in July 1943, because of an explosion and fire in the tank farm area.

Also it will be noted that after the bombing on July 31, 1944, production fell off rapidly and that subsequent bombings finally stopped production on December 15, 1944. See Monthly production table.

Ludwigshafen can produce only enough ethylbenzene to make 500 tons of styrene per month. They can produce another 500 tons of styrene by importing 500 tons ethylbenzene from Schkopau.

Equipment for producing butadiene was never completed, but present capacity is probably only sufficient for 20,000 tons Buna S-3 per year.

The Buna S polymerization plant was laid out for 48 reactors in 6 lines of 8 each. Of these only 40 were installed. Of the latter 16 were removed last year probably for use elsewhere and also because polymerization capacity was considerably too large for the rest of the plant. Using the formula and reactor rate employed in Germany, the remaining 24 are ample to produce 30,000 tons

annually, leaving 4 reactors always in reserve. Using the American formula and rate, these reactors could produce 50,000 tons providing cooling area is adequate.

The Buna S finishing lines are estimated capable of handling 35,000 tons output.

-Metric Tons

Monthly Production 1943 Metric Tons

	Buna S-III (First Quality)	S V (Off Grade)	S A (Scrap)	TOTAL
March				153
April	(No breakdown)			508
May				738
June				824
July				430
August				806
Sept.				575
Oct.	524	82	65	671
Nov.	907	109	135	1,151
Dec.	1,293	29	3	1,325
Total	2,724	320	203	7,181

1944

Jan.	1,030	39	55	1,124
Feb.	1,034	93	21	1,148
March	1,842	151	21	2,014
April	1,534	128	27	1,689
May	1,616	75	29	1,720
June	1,592	111	24	1,728
July	1,437	190	16	1,643
August	0	258	182	440
Sept.	121	4	46	184*
Oct.	20	1	0	46*
Nov.	67	10	1	94*
Dec.	82	4	33	126*
Total	10,375	1,064	455	11,955

* Including approximately 20 T monthly Buna latex.

Processes

It was found that all German plants except Ludwigshafen used the well-known aldol process for butadiene manufacture. Ludwigshafen, however, based its manufacture on the Reppe synthesis which involves (1) the reaction of formaldehyde and acetylene to form butindiol, (2) hydrogenation of this to form 1,4 butandiol, and (3) dehydration of the latter to butadiene. This process is not as economical as the aldol process because it utilizes formaldehyde from methanol. Individual yields for each step, however, are good.

In the manufacture of styrene, ethylbenzene is formed by the continuous alkylation of benzene with ethylene in the presence of aluminum chloride. Styrene is made by dehydrogenation of ethylbenzene over zinc oxide base catalyst in the presence of steam.

In the manufacture of Buna the two hydrocarbons are mixed together in the proportion of 70 parts butadiene to 30 parts styrene, are then emulsified using a sulfonated naththalene 100 parts of hydrocarbon to 106 parts of water. Polymerization is continuous through 7 reactors connected in series to give 62% conversion in 30 hours. Recovery losses are high. Coagulation is achieved without the use of tanks using sodium and calcium chloride with a small amount of acetic acid. The crumb is formed into sheets on a fourdrinier machine and dried in a 19 pass drier divided into three temperature zones. The final packaged rubber consists of uncompressed rolls weighing 100 Kgs.

Koresin is made by reacting acetylene with isobutyl phenol in the presence of zinc naphthenate. Isobutyl phenol is made by continuous alkylation of phenol with isobutylene derived from isobutyl alcohol.

Details of these processes will be found in Part II of this report.

Raw Material Requirements and Process Yields, Ludwigshafen.

From Document 1814-4d.

Requirements for 30,000 Tons per year (8766 hours)

Material	Yield % of theory	Required per 100 Kg Buna S-3.	Required for 3422.3 Kgs/hr Buna S-3.
Styrene		30.2 Kg	1034
Butadiene 100%		73.8 "	2528
Butandiol 98.3%	90.0%	139.3 "	4770
Butandiol crude	97.2%	143.2 "	4908
Butindiol crude	93.0%	147.1 "	5040
Formaldehyde 100%	92.0%	111.6 "	3820
Acetylene purified 100%	92.0%	48.3 "	1655
Acetylene crude 100%	95.5%	50.6 "	1732
Carbide (283.6 litrig)*	96.0%	169.0 "	5790

* Cu.m. of acetylene generated per ton.

Coal Requirements

From Document 1814-23.

Total coal requirements are said by Dr. Niemann to be 17 tons per ton Buna S-3.

Location and Condition of Plant.

Out of the 860 buildings composing the I.G. Chemical Works at Ludwigshafen and Oppau some 20 are essential to the manufacture of synthetic rubber and its raw materials. These buildings, with a description of their condition at the time of our visit, together with their LU number by which they can be located on any I.G. plant plan, are as follows:

LU No.	Description	Condition
257	Power Plant	1 of 4 boilers operable. Adequate to operate plant at 50% capacity.
432	Carbide Furnaces	Half damaged, rest operable.
453	Acetylene Generators	" " " "
137	Acetylene Scrubber	" " " "
186	Formaldehyde Plant	Lightly damaged.
128	Butindiol reactors	" "
134	Butandiol "	Six out of eight destroyed.
158	Butin - and Butandiol columns	Half damaged, half operable.
165	Tank Storage	Largely destroyed.
167	Butadiene reactors	Half destroyed, half operable building badly damaged.
166	Butadiene columns	One set badly damaged, other operable.
157	Tetrahydrofuran plant	Partially damaged.
171	Butadiene Compressors	Very little damage.
615 (N.half)	Ethyl Benzene	Severely damaged, not reparable.

LU No.	Description	Condition
614	Styrene reactors	Severely damaged. Only 2 of 11 reactors reparable.
193	Buna polymerization	Lightly damaged, easily reparable.
195	Coagulation and finishing	Lightly damaged, easily reparable.
117	Water purification	Lightly damaged.
114	Intermediates synthesis (Isobutyl phenol)	Building damaged, equipment could be restored.
926	Koresin reactors	One of three destroyed, rest easily repaired.

C.I.U. MOSAIC Nº 1186

LUDWIGSHAFEN - OPPAU

I.G.F. CHEMICAL WORKS

0 500 YARDS APPROX

Neg. Nº 23315

SYNTHETIC RUBBER PLANT
(see key to building numbers)

The following figures were extracted from Document 1814-4d, dated 31 January 1945:

At Ludwigshafen		
Manufacturing costs for the best quarter (2nd quarter 1944)	229.42	Reichmarks per 100 Kg.
With full production of 30,000 tons/year under present conditions.	206.75	"
With present equipment, but under normal peacetime conditions.	169.34	"
Most optimistic cost assuming continued progress.	159.00	"
At Schkopau		
Present manufacturing cost.	⁂ 130.00	"
Natural Rubber	70.00	"

⁂ Source of this information not given.

Direct Operating Personnel, July 1944.

	German		Foreign		Total
Butadiene Manufacture	Men	Women	Men	Women	
Carbide Plant	70	6	83	36	195
Acetylene Generator and Purification	25		26		51
Butindiol	48	8	10	15	81
Butandiol Preparation	36	25	7	13	81
Butandiol Distillation	30		11	11	52
Butadiene Operators					86 *
Catalyst cleaners					62 *
Buna Manufacture					
Polymerization	45	13	14	27	99
Finishing	28	8	6	73	115

Lost Time in Buna manufacturing Dept. expressed as per cent of total man hours worked.

Cause	Germans	Foreigners
Sickness	14	7.7
Vacation	5.5	1.6
Leave of absence	1.6	-
Arrest	-	4.4
Other causes	.9	2.0
Total	22.0	15.7

* obtained by dividing total manhours per month by 200. (17,311 operating, 12,438 catalyst cleaning)

o taken from document 1814-15c.

In November 1942, a planned program was set up for the production of Buna in Germany. This is covered in detail in Document 1814-12 which also shows the progress made on the program in 1943. This program required some addition to each of the plants, mostly removing bottlenecks, and an appreciable increase of labor, which was apparently a difficult problem.

The following tabulation shows the existing production capacity at the end of 1942 and the planned capacity of the finished program:

	Tons/mo Nov.1942.	Tons/mo Finished program	Estimated completion date
Schkopau	5000	5000	completed
Huls	3300	4150	end of 1943
Ludwigshafen	0	2500	end of 1943
Auschwitz	0	2500	Spring 1944
Ferrara (Italy)	0	1000-1500	Spring 1944
Leverkusen (Buna N)	250-500	250-500	

The speed of completing the program was apparently quite important due to urgent 1943 military requirements and two sets of estimated productions in 1943 were prepared, one assuming normal installation rate and the other an emergency program expedited to the limit. The Buna S production, excluding Italian, was therefore set forth as follows for 1943:

Production in Tons/month

Normal Program	Schkopau	Huls	Ludwigshafen	Total
1st quarter 1943.	5000	3300	300	8600
2nd " "	5000	3300	900	9200
3rd " "	5000	3550	1500	10050
4th " "	5000	3800	2000	10800

Emergency Program	Schkopau	Huls	Ludwigshafen	Total
1st quarter 1943.	5000	3550	300	8850
2nd " "	5000	3550	1650	10200
3rd " "	5000	3800	2500	11300
4th " "	5000	4050	2500	11550

Now that we have obtained actual production figures from these three plants, a comparison showing by what amount they failed to meet this program is interesting.

Actual Production in Tons/month

	Schkopau	Huls	Ludwigshafen	Total
1st quarter 1943.	5416	3754	51	9221
2nd " "	5409	3409	688	9506
3rd " "	5752	845	603	7400
4th " "	5956	3389	1049	10394

Total production for 1943 was:

Schkopau	67,703 tons
Huls	34,293 "
Ludwigshafen	7,177 "
	109,173

German Buna Production 1944.

On a map dated Nov. 18, 1944, found in Dr. Ambros' office, the following production forecast and plant capacities as of that date are given:

Plant	Estimated Production tons per month.	Capacity of completed plant
Ludwigshafen	2,000	2,500
Schkopau	6,000	6,000
Huls	1,750	3,500
Auschwitz	2,000	2,000
	11,750	14,000

This would indicate an attained capacity of 140,000 tons per year against a planned capacity of 170,000. Actually the first figure was never reached since Ludwigshafen produced in 1944 only 12,000 tons and Auschwitz never operated. German production during 1944 was probably not more than 112,000tons.

Summary of Process, Costs and Yields.

It was found that butadiene was manufactured at Ludwigshafen by an entirely new method called the Reppe process. Briefly this synthesis consists of reacting two mols of formaldehyde with 1 mol of acetylene to form butindiol, hydrogenating this to 1,4 butandiol and dehydrating the latter to butadiene. However the details of this process are quite involved and there are many intermediates and by-products formed. It appears from the various documents that this process was difficult to get into operation and that the cost of butadiene, even under most favorable post war conditions will not compete with that made by the well-known aldol process used at Huls, Schkopau and Auschwitz.

No actual costs were obtained for Ludwigshafen production of butadiene, but the following table is of interest as the estimate made in 1941 for this process:

	Yield % of theory	Tons Req'd for 24000 T Buna/Yr	Cost in RM/Kg (a) Cost with Leuna methanol	Cost in RM/Kg (b) Cost with Oppau Methanol	Cost as in (b) except with lowered power cost
Carbide	-	-	11.95	11.95	-
Acetylene	-	11,300	44.25	44.25	40.00
Formaldehyde	-	24,600	30.00	20.00	20.00
Butindiol	95% from CH_2O				
	92% " C_2H_2	34,200	42.31	35.11	32.45
Butandiol	93%	34,400	50.81	43.64	40.20
Tetrahydro-furan	96%	27,000	67.48	58.34	53.95
Butadiene	93%	19,200	106.78	93.94	86.67

This butadiene cost may be compared with Schkopau 1943 cost of 115 RM/Kg. Since the actual yields so far at Ludwigshafen have been distinctly lower than the above, the costs have been correspondingly higher. Whether it would ever be possible to attain the above figures is, of course, impossible to say due to lack of sufficient operating information.

PART II

TECHNICAL

The main steps in the process may be summarised by the following chemical reactions:

Step I $CH_2O + HC \equiv CH + CH_2O \rightarrow CH_2OH - C \equiv C-CH_2OH + 55$ K cal.
(4.5 atm., 100-120°C, copper acetylide catalyst)

Step II $CH_2OH-C \equiv C-CH_2OH + 2H_2 \rightarrow CH_2OH-CH_2-CH_2-CH_2OH + 60$ K cal.
(300 atm., 120°C, copper nickel catalyst)

Step III $CH_2OH-CH_2-CH_2-CH_2OH \rightarrow CH_2=CH-CH=CH_2 + 2H_2O - 23.5$ K cal.
(1 atm., 280°C, sodium phosphate catalyst)

As an intermediate product of dehydration tetrahydrofuran is formed by the loss of one water from 1,4 butandiol. This step results in the release of 3.2 K cal./gm. mol. Further dehydration to butadiene takes place with the absorption of 26.5 K cal./gm. mol.

It is believed that this process was put in as a war emergency program in order to utilize available methanol from Leuna and to make unnecessary a large expansion of carbide facilities and the corresponding power plant. The process does not look very interesting for butadiene manufacture, but may have important applications in the production of other chemicals.

Of particular interest in assaying the Reppe process is the yield of desired material in each step as compared with theory. This process is new and hence results obtained at Ludwigshafen are not too reliable, particularly in view of heavy bombing effects. The following tabulation shows several compilations of available information:

	Basis % of theoretical yield on each step					
	Stated by Dr. Niemann	Memo 31/1/45 Doc. 1814-4d (Est. of future)	July 1944	Aug. 1944	Sept 1944	Lab. scale Doc. 1814-20	Pilot plant scale
Carbide to raw acetylene		96.0	91.1	88.4	86.0		
Raw acetylene to pure acetylene		95.5	93.4	94.9	96.6		

	Basis % of theoretical yield on each step						
	Stated by Dr. Niemann	Memo 31/1/45 Doc. 1814-4d (Est.of future)	July 1944	Aug. 1944	Sept 1944	Lab. scale Doc. 1814-20	Pilot plant scale Doc. 1814-20
Pure acetylene to butindiol	90	92.0	77.2	75.4	94.5	92	92
Pure formaldehyde to butindiol	90	92.0	90.7	88.8	92.4	97	95
Butindiol to Butandiol	90	93.0	94.6	96.0	95.4	96	93
Butandiol purification		97.2	97.2	97.7	97.2	98	98
Butandiol to 100% butadiene	90	90.0	84.4	83.1	84.7	95	93
Butadiene purity %	99+		(98.0)	(98.1)	(98.4)		
Overall yield acetylene to butadiene	73	75	60	59	74	83	78
Overall yield formaldehyde to butadiene	73	75	71	69	72	87	80

Apparently the last step (butandiol dehydration) has never worked out as well commercially as was expected from laboratory work.

Introduction

The Ludwigshafen butadiene process is a development from general researches under the direction of Dr. Reppe leading to studies of acetylene chemistry. This was reported in Dr. Reppe's manuscript (Doc. 1814-19) on July 26, 1940. In addition to a new butadiene synthesis from formaldehyde and acetylene, Dr. Reppe describes the synthesis of many other compounds such as Koresin and other vinyl derivations suitable for synthetic rubber, leather, paper and fabric coatings.

This early work (about 1937) was followed by a report (Doc. 1814-24) dated 6/9/40 discussing particularly the butadiene synthesis. On Jan. 24, 1941, Dr. G.Niemann reported results on pilot plant work on this new process at Ludwigshafen (Doc.1814-20) and described in general how the large plant would be constructed and the estimated costs and yields. On 12/5/44 Dr. Niemann made an address before the inorganic colloquium describing the actual operations at Ludwigshafen and some of the future possibilities of the Reppe synthesis (Doc. 1814-23). These documents, together with results of interrogation of Dr. Niemann and other documents found in Dr. Niemann's files relating to actual productions, yields, costs, etc., give a rather comprehensive picture of the entire process.

The first steps are the production of acetylene from calcium carbide and formaldehyde from methanol brought in from Leuna. It was planned later to make methanol at Oppau in the units now used for ammonia synthesis which would reduce somewhat the cost of butadiene. The formaldehyde and acetylene are reacted in the presence of copper acetylide catalyst to form butindiol. This after purification is hydrogenated at high pressure to 1,4-butandiol and the latter, after purification, is dehydrated over phosphate catalyst to produce butadiene. These steps in general go fairly well according to theory, but there are appreciable mechanical and separation losses. Many of the details of the process steps are shown in the various documents so attention here will be paid to the more important phases of the process as applied at Ludwigshafen.

Carbide Manufacture (Bldg 432)

Carbide is manufactured by the usual three phase electric furnace method. There are two furnaces, each having a capacity of 4000 T carbide per month. The charge of lime, coke and coal is crushed and fed continuously into the top of the furnaces in the desired proportions. The furnaces are rectangular with water-cooled electrodes and sides. The carbide is formed at about 2500°C and tapped at 1800°C into a horizontal cooling pipe 2 m. dia. and 43 m. long before being crushed for acetylene generation. It is then stored over N_2.

A review of this plant for the first 8 months of 1944 shows the following material balance:

Input			Output	
Lime	34,321 tons.		Carbide	35,308 tons.
Coke	13,116 "		* Gas	8,148,09 m^3
Coal (anthracite)	7,268 "			
	54,705 "			

* analysis 56.7% CO, 15.7% H_2, 4.4% CO_2, 23.2% N_2.

It will be noted that the production is considerably less than capacity during this period as only one furnace was operated part of the time. The power consumption on the carbide plant was found only for one month and was shown as 3,148 KWH/T carbide.

Acetylene generation and washing (Bldg 453, 137)

Acetylene is generated by carbide in horizontal rotary drums with the carbide flowing counter-current to water spray. There are duplicate facilities for this as well as for acetylene washing. The raw acetylene gas is removed and the calcium hydroxide finished for fertilizer.

The gas is cooled and freed from dust, etc., by water washing and by washing with dilute HCl. It still contains a trace of ammonia, 380 mg/m^3 of phosphorus and 1600 mg/m^3 of sulfur compounds which are removed in two sets of four washers 1.8 m. diameter and 11 m. high each. The ammonia is washed out with dilute H_2SO_4 in the first tower and sulfur and phosphorus removed by washing with sodium hypochlorite or chlorine water in the next two towers. The last tower is used for treatment with dilute NaOH. The gas then goes to a coke-filled separator to remove entrained liquids.

The raw acetylene is further purified to remove traces of sulfur and halogen compounds in two sets of three absorbers containing activated carbon. Two absorbers are used at a time and one is on regeneration with steam and heated acetylene.

Formaldehyde Manufacture (Bldg 186)

Methanol from Leuna is diluted to 60% and vaporized with low pressure steam. Air is added to make a vapor of methanol, steam and air at 90°. The vapor is then heated to 600° and passed over a catalyst and cooled stepwise. It is then washed several times in bubble towers with condensate water to form 30% formaldehyde solution which is then stored in aluminum tanks. Details of this process were not obtained.

Butindiol manufacture (Bldg 128 and 158)

Acetylene from carbide and 30% formaldehyde solution are used for the preparation of butindiol in the presence of copper acetylide catalyst at a temperature of 100-120° and 5 atm. pressure. It was originally contemplated to install eight continuous reactors in parallel but only six were actually installed. These reactors were each 1.5 m dia., 18 m high and 30 m^3 in volume, housed in separate explosion bays and fabricated out of V2A metal to withstand 100 atm. pressure. This was done to allow for possible explosion of

acetylene and copper acetylide. The reactors were equipped with several liquid redistribution cones at various levels.

In actual operation, however, in order to obtain complete conversion of formaldehyde in one pass, and to prevent too high temperature rise during the reaction it was found necessaty to use two reactors in series to keep the formaldehyde solution dilute and to use at least four times the theoretical acetylene. Feed temperatures were also kept fairly low. Eventually two reactors were taken out to act as water recovery units for the reactor product gases and the other four were used as two sets of two in series for the reaction.

About 12 m^3 of fresh 30% formaldehyde solution per hour was used for the entire operation. This was diluted to 40 m^3 by (1) addition of 4 m^3 as dilute formaldehyde and propargylalcohol from the distillation train; (2) 23 m^3 by water pickup from the reactor product gases. Thus a 15% formaldehyde solution was actually fed with four times theoretical acetylene to the top of two of the reactors. Both gas and liquid then passed down through these reactors over the catalyst (copper acetylide on silica carrier), where the reaction was carried to the point where the formaldehyde concentration was 5%. The flow was then down through the next two reactors where the formaldehyde concentration was reduced to 1.5% or less (usually 0.5% or less). Overall conversion of formaldehyde was 95-98% in the one pass through the two sets of two reactors in series. The ultimate yield on formaldehyde was around 90% although laboratory data indicated 95-97% should be obtained.

The 40 m^3 of formaldehyde feed per hour was treated with sodium bicarbonate to maintain Ph 4-5 and was split into four streams of 10 m^3 each. Two streams were used for feed to the two sets of reactors and the other two streams were used to pick up water from the reactor product gases. The reactor products passed to a separator and the separated gas scrubbed in the water pickup reactors to remove a large part of the water from the gas stream. The stripped gas, consisting largely of acetylene, but containing methanol, propargylalcohol and water was cooled further to condense out the remaining liquid products. Both directly separated liquid and condensate from the cooler were mixed and sent to the purification train.

The acetylene released from the separator was recycled to the reactors by means of Elmo pumps having a capacity of 350 m^3 per hour each. Fresh acetylene was compressed to four atmospheres and then added to the recirculating stream. About 1000 m^3 per hour of

acetylene was circulated per reactor set. The circulating pumps as well as all other apparatus in the reactor system were designed for 100 atm. pressure.

Laboratory data indicated that about 1 Kg butindiol could be produced per liter catalyst volume per day at a velocity of 3 Kg pure formaldehyde per square decimeter cross-sectional area per hour. Thus each of the four reactors produced about 30 T butindiol per day. The catalyst preparation is discussed below under catalysts, but essentially the material is copper acetylide on silica carrier, and the catalyst life is about two months.

The crude butindiol was purified in four fractionating columns. In the first column methanol, propargylalcohol and unreacted formaldehyde were taken overhead at 1.5 atm., 120° top temperature and 128° bottom temperature. The 38-40% butindiol water solution was then sent to the hydrogenation plant for conversion to butandiol. The overhead from the first column was fed to a second column operating at atmospheric pressure, 63° top temperature and 92° base temperature. This column removed crude methanol overhead and propargylalcohol and formaldehyde water solutions (7% concentration of each) from the bottom. The latter was recirculated to the formaldehyde feed tanks or was distilled in the third column to take a 30% propargylalcohol solution overhead and a formaldehyde solution below, which was recirculated. By sending part of the solution from the second column through the third column propargylalcohol was continuously withdrawn from the system. The fourth column was used to purify the crude methanol by batch distillation at atmospheric pressure and 67° base temperature.

It will be noted that a small amount of propargylalcohol is produced as a by-product in this reaction and is due to the reaction of 1 mol acetylene with 1 mol formaldehyde. By suitable changes in conditions the reaction can be made to go largely to this alcohol which is a useful intermediate for the manufacture of other chemicals.

Butandiol production (Bldg 134 and 158)

Butandiol is produced by the hydrogenation of 35-40% butindiol solution with H_2 at 300 atm. in the presence of copper-nickel on silica catalyst. The feed enters at 20° and leaves at 120°. The set-up consists of seven high pressure reactors in parallel of which five are used for hydrogenation and two for hydrogen purification. Each reactor is 0.8 m diameter and 18 m high.

The butindiol and hydrogen (after preheating) are sent to the top of the reactors. Since the reaction is highly exothermic (60

K cal per mol), 80 times the theoretical hydrogen is circulated through the reactors, requiring a circulation of 75,000 m^3 H_2 per hour. The product liquid and gas are passed to a heat exchanger, cooler, and separator where hydrogen is separated for recirculation. The liquid product contains 35-40% butandiol, 1-2% butanol and remainder water. The butanol yield gradually increases as the catalyst gets older. The catalyst list if 1 to 3 months and the production is 4 Kg butandiol per liter catalyst per day. The used catalyst is sold for metal recovery.

Two reactors are used to purify hydrogen which is made at Oppau. This gas contains 0.05% CO which is removed catalytically at 280°C over nickel catalyst to a CO content of 0.001%.

The butandiol solution is purified in 7 bubble columns. The first column operates at atmospheric pressure to remove butanol overhead. The second column removes the larger part of the water overhead leaving a concentrated butandiol solution. This is used either for tetrahydrofuran manufacture or is purified in the remaining columns under reduced pressure. The third column operates under vacuum to remove practically all water overhead. The fourth column removes a dilute butandiol overhead which goes to the fifth tower to concentrate the butandiol. The butandiol from the base of the fourth column and from the fifth column are joined and distilled overhead in the sixth column. The last column is used batchwise to remove traces of butandiol from residue. Conditions in each column are as follows:

		Temperature		
	Press.	Top	Bottom	Operation
1. Butanol column	760 mm	92°	100°	Continuous
2. Water column	760 mm	100°	112°	"
3. Vacuum-water column	80 mm	56°	165°	"
4. Crude Forecolumn	50 mm	145°	175°	"
5. Pure Forecolumn	40 mm	143°	175°	"
6. Pure Butandiol column	20 mm	115°	180°	"
7. Residue column	5 mm	110°	185°	Batch

Butadiene production (Bldg 167 and 166)

Butadiene is made from butandiol by dehydration at 280°C and 1 atm. over sodium phosphate on coke catalyst. The first step in dehydration is to tetrahydrofuran with the release of 3.2 K cal/gm mol and this is then further dehydrated to butadiene with the absorption of 26.5 K cal/gm mol. Thus either tetrahydrofuran or

butandiol can be used as feed for the final step. In fact, at Ludwigshafen, a separate plant to produce tetrahydrofuran from butandiol was installed (see below) using a different process for the dehydration, in order to tell whether it was desirable to dehydrate in one or in two steps. Since tetrahydrofuran is an intermediate product, which is readily formed, the materials actually undergoing reaction consist largely of this substance. It is not clear whether an equilibrium mixture of butandiol and tetrahydrofuran actually is formed or whether the reaction is almost immediate and quantitative to the furan.

The heat absorption problem in this step is quite difficult because of the use of large granules of coke catalyst. The 12 reactors used at Ludwigshafen are similar to the ones used for 1,3 butylene glycol at the other plants and are vertical cast iron cylinders, insulated on the outside and containing 20 m^3 of catalyst. The reactors are made in segments which are stacked on top of each other, and joined by gasketed flanges. Between each segment and across the entire section of the reactor (except near the center where a graphite plug is inserted) is placed a pancake coil to heat the catalyst bed with 100 atm. steam. This steam is produced by flue gas and electrical resistance heaters. The segments of the reactors are about 1 foot apart. The reaction is carried to 20% per pass and the catalyst life is about 3 weeks, being limited by pressure drop increase.

The butandiol is vaporized with steam. Tetrahydrofuran is also separately vaporized and mixed with butandiol vapor and steam in heat exchange against the hot reactor products and heated to 200°. The mixed feed is further preheated to 330° with 100 atm. steam and an electrical resistance superheater. The gases enter the base of the reactor at 320° and the pancake coils maintain the temperature at about 280°. The space velocity is about 0.5 Kg butadiene per liter catalyst per day. Pilot plant work indicates that the feed to the reactors consists of 2.1 mols butandiol, 7 mols steam and 8.7 mols tetrahydrofuran with the product containing 2.0 mols butadiene, 8 mols steam and 8.7 mols tetrahydrofuran. Thus the reaction is one, in effect, of dehydration of butandiol in the presence of steam with tetrahydrofuran acting as an intermediate product and diluent. Some net conversion of furan takes place also because of the fact that this material is also added to the feed from the tetrahydrofuran plant.

The crude stream containing largely water, tetrahydrofuran and butadiene is sent to one of two duplicate distillation trains after passing in heat exchange against the feed. The first column removes water from the base and tetrahydrofuran is trapped out from near the top of the column. From the top of this column is taken a mixture of butadiene and a little tetrahydrofuran which is washed with dilute caustic potash in a tower and taken through a 500 cu.m gasometer to compressors. The gas is compressed to 3-5 atm. and sent to a separator to remove gas. The liquid butadiene-tetrahydrofuran mixture is dried over solid caustic and then taken to the pure butadiene column to remove butadiene overhead and tetrahydrofuran from the base. The butadiene is condensed with water. The tetrahydrofuran recycles to the first column for purification and eventually returns to the tetrahydrofuran vaporizer.

Tetrahydrofuran Manufacture (Bldg 157)

As an integral part of the Reppe process tetrahydrofuran is manufactured at Ludwigshafen from the 35-40% crude butandiol. This solution is freed from salts and neutralized with Wofatik K (a hydrogenion exchanger) which can then be regenerated with HCl. The salt free solution is then brought to P_H 2.0 with 0.3% phosphoric acid, preheated to 300° and sent to four parallel reactors at 100 atm. and 290°C where it is converted to tetrahydrofuran. Sulphuric acid can also be used in place of phosphoric acid. The reactors are 1.0 m. dia. and 15 m long and are made of V2A. The space velocity is 4 Kg tetrahydrofuran per liter catalyst per day.

The reaction is homogeneous in the liquid phase and is substantially quantitative with the release of only 3.2 K cal/gm. mol. Actual yields of 90-94% have been obtained in the plant. The product can be used for manufacture of other chemicals or can be charged as part of the feed to the butandiol dehydration step. The solution is sent to a heat exchanger and then to an atmospheric pressure tower which takes overhead the azeotrope of tetrahydrofuran and water (6% H_2O) at 64° and residue and water below.

Butadiene catalyst manufacture

A number of documents were found describing the manufacture and use of the various catalysts used in

the butadiene synthesis. These documents were supplemented by verbal statements by Dr. Niemann. It is believed that the following is a fair summary of these methods:

(a) Catalyst for butindiol production from acetylene and formaldehyde.

This catalyst is apparently copper acetylide on an inert carrier (silica). The active ingredient is either $Cu-C_2$ or $Cu_2C_2-H_2O-C_2H_2$. The catalyst contains 12.5% Cu, 3.5% Bi and remainder silica prepared as shown under (b) below. The size is 2-6 mm and the bulk density 0.55. The calcined silica pellets are saturated with a solution of copper and bismuth nitrates, then dried and heated in a muffle to 500°. The catalyst is placed in the reactor and treated with formaldehyde and acetylene at a temperature of 50-100° (70° best). By being careful to saturate the catalyst with formaldehyde solution first, adding acetylene slowly and bringing the temperature up slowly, the catalyst is changed to the active acetylide. It is then raised in temperature to reaction temperature and butindiol production begun.

The catalyst is, of course, subject to detonation, as is acetylene itself. Special precautions are necessary to prevent explosion which are described in various documents. If the temperature is raised above 120° cuprene is formed which coats the catalyst and renders it inactive.

(b) Catalyst for the hydrogenation of butindiol to butandiol.

This catalyst is basically copper-nickel on an inert carrier (silica). The final product contains 16 parts nickel, 5 parts copper and 0.7 parts manganese added as an activator. This is made as follows:

Sodium silicate is put into a stirred vessel and dilute H_2SO_4 run in below the stirrer. The preciptate is filtered in a filter press, dried in a drum drier, ground and made into paste in a pug mill. The product is extruded in cylindrical form, dried and heated in a rotary kiln. The calcined pellets are impregnated with the nitrates of the above salts, dried and heated in a kiln to 450°. The particles are then screened on a vibrating screen to remove fines. The catalyst, after

being placed in the reactor is treated for 24 hours at 320° and 50-100 atm. with H_2 for reduction to the active metals. Some lessing rings of Cu and of Ni are also added apparently. The use of nickel instead of only copper as is used for aldol hydrogenation prevents a large formation of butanol, but requires a purer hydrogen.

(c) Catalyst for the dehydration of butandiol to butadiene.

This catalyst is basically sodium phosphate on a coke carrier. The catalyst was stated to contain 15% mixed sodium hydrogen phosphate, but this is apparently incorrect as noted below. It is made as follows:

Coke is broken into 8-15 mm granules by crushing and sizing hydrogen phosphate and butylaminephosphate solution. The coke is sprayed in a rotary drum with sodium. The water is then evaporated by direct contact with flue gases. The impregnated particles are dried and heated to 260° in a tunnel kiln to transform the Na_2HPO_4 first to $Na_2H_2P_2O_7$ and then finally to 80% $(NaPO_3)_2$ and 20% $Na_2H_2P_2O_7$. This catalyst is the same as for the dehydration of 1,3 butylene glycol to butadiene except that it is more completely converted to $(NaPO_3)_2$. It will be noted that the stated 15% concentration on the catalyst is at variance with the 45 parts per 100 parts catalyst indicated in Document 1814-20, and as shown later from Huls and Schkopau information. Reference should be made to the reports on these plants for more exact information.

The spent catalyst, after 3 weeks use, develops too much pressure drop and is then removed and screened into powder and granules. The solution is leached out of the granules with hot water in a 8 cu.m. vessel. The powder is leached separately in a similar manner and then separated by filtration. The solutions recovered are concentrated in evaporators and re-used.

Comparison of Reppe process with aldol process.

A number of documents were obtained at Ludwigshafen relating to Schkopau operations. These will be discussed in the Schkopau report. It is, however, of some interest

to compare the Reppe butadiene process with the aldol process used at Huls, Schkopau and Auswitsch plants.

The overall yield of butadiene by the aldol process is 60% of ~~theory based~~ on acetylene or 64% based on acetaldehyde. The Reppe process at Ludwigshafen yielded 71% of theory (based on formaldehyde) in the third quarter of 1944, and earlier research indicated 80-87%. Dr. Niemann estimated normal plant yield would be about 75%, under peacetime operating conditions. It may therefore, be concluded that the Reppe process would give somewhat better yields than the aldol process as carried out in Germany, that it would save the necessity of installing large blocks of power equipment, but that the investment and operating costs are not likely to be low enough to permit production of butadiene as cheaply as by the aldol process. This conclusion is shared by the Huls and Schkopau operators.

Production Statistics

No comprehensive reports were found relative to the production of butadiene and intermediates except for the third quarter of 1944. These are as follows:

	July	Aug.	Sept.
Acetylene	899,000 m^3	412,770 m^3	106,945 m^3
Butindiol	2,167.9 T	896.0 T	295.0 T
Butandiol	2,065.8 T	828.2 T	303.9 T
Butadiene	1,323.7 T	394.6 T	167.3 T
Butadiene purity	98%	98.1%	98.4%

Production for previous months may best be judged from Buna production statistics, since butadiene was the apparent bottleneck item.

Ethylbenzene Production (Bldg 615)

The production of ethylbenzene at Ludwigshafen could not be studied very completely because of the general state of the equipment and the absence of adequate German technical personnel on this subject. A brief study indicated, however, that ethylene was produced from ethyl alcohol by dehydration over CaO. This, together with purified benzene was fed to two continuous parallel reactors, enamelled lined and 1 m. diameter and 6 m. high. Later information indicates that the system used was the same as that used at Schkopau and essentially the same as at Huls. Original work on this process was carried out at Ludwigshafen. Reference should be made to the reports on these targets for more precise information on the process.

The reactors are vertical cylinders and provided with inlets at the base for ethylene, benzene and recycle aluminum chloride complex. The mixture passes upward at 80° C and 1 atm. and overflows to a separator, where the complex is returned to the reactor and the alkylated liquid removed for washing and distillation. $AlCl_3$ is added at the top by means of a screw conveyor. The reactors are jacketed to permit cooling or heating as desired. It was stated that the $AlCl_3$ use was 50-100 Kg/1000 Kg ethylbenzene produced. The product from the reactor contained 40% ethylbenzene, 10% polyethyls and 50% benzene and the overall yield was stated to be 90% of theory. These figures should be accepted with reservation.

The two reactors have a total capacity of 500 T ethylbenzene per month. To this was normally added 500 T/month from Schkopau in order to take care of Buna S and Polystyrene requirements.

The washed crude ethylbenzene is distilled to separate unreacted benzene, ethylbenzene, polyethyls and residue. It was stated that the first tower removed benzol overhead and the second tower removed pure ethyl-benzene overhead and polyethyls and residue from base. The bottoms are then redistilled to remove polyethyls overhead which are returned to the alkylation units together with unreacted benzene. More complete details on this distillation train can be obtained from Huls information.

Styrene is produced by catalytic dehydrogenation of ethylbenzene in the presence of steam. The exact steam usage was not stated definitely, but data from a process flow sheet indicated that 2 lb of steam was used per lb of ethylbenzene. The reaction was carried out in vertical multitubular reactors with tubes about 4" diameter. The composition of these tubes was stated to be chrome-manganese, but this appears in error in view of later data at the other plants.

The catalyst used in the reaction was stated to be mixed oxides of zinc, calcium and aluminum with added promotors, but it was not possible to obtain the exact composition or method of manufacture since the expert on this (Dr.Ohlenger) was absent from the plant for several days.

The ethylbenzene and water are vaporized and preheated to reaction temperature (about 600°) by means of heat exchange against the flue gases used previously for heating the reactor tubes. The mixture then flows down through the reactor tubes which are filled with catalyst. Conversion takes place to the extent of 40% per pass and an ultimate yield of 90% of theory is obtained. The reaction proceeds continuously, with coke formation being removed by the water gas reaction, so that no periodic regeneration is required. The catalyst life was stated to be 9-12 months. The reactor tubes are heated by burning gas in air and circulating the hot flue gases around the reactor tubes to maintain approximately 600°.

The reactor product gas is sent to a condenser and cooler and the gas separated from the liquid. The liquid condensate is then settled to separate water and insoluble oils and dust before being purified in a distillation train. The water is returned to the reactor system.

The Ludwigshafen plant has a total of 11 reactors of which 10 were kept in operation, each having a monthly capacity of 100 tons. Thus 1000 T/month could be made using ethylbenzene from current production as well as shipments from Schkopau and at times from Huls.

No details of the Ludwigshafen styrene distillation train were obtained. Apparently 3 towers were used in total. One tower, operated under vacuum, removes ethylbenzene overhead which is recirculated to the dehydrogenation step. The second tower, also

under vacuum, removes pure styrene overhead and residue from the base. The styrene is stated to be 99.7-100% pure and is used directly without inhibiting unless it is stored for a long time. In this event hydroquinone is added in small amounts. It is suggested that since the process is quite similar at the other plants, more details on this system can be obtained from the Huls report.

Polystyrene Production at Ludwigshafen (Bldg 615)

Styrene monomer is fed to the top of a vertical tower 25' high by about 24" diameter filled with spiral steam coils. The tower is operated full and the contents are maintained at a temperature of 190° C throughout. At the base polymerized styrene is extruded through a narrow horizontal slot about 1" long by mild pressure exerted by a horizontally disposed screw feed. Polymerization time is regulated by the rate of extrusion. Average time was stated to be 30 hours. The extruded strip falls on a horizontal travelling steel belt running over and under cooled rollers for a distance of about 20 ft. at the end of which the cooled strip of polystyrene is fed to a rotary knife which reduces it to particles about the size of rice grains.

In this condition it feeds by gravity to a hammer mill which reduces it to a coarse powder, in which form it is packed in resin treated bags for shipment.

The original plant was destroyed by bombing but has been rebuilt to produce about 100 tons per month out of two sets of towers, cooling strips and pulverizers of the type described above. No catalyst or other chemicals are used.

Types

Synthetic rubber manufactured at Ludwigshafen which meets their specification (Defo hardness = 3000 ± 10%) is called Buna S-3. It is produced as an uncompressed thin sheet and is rolled up on a central spindle to about 100 lb rolls.

Rubber failing to meet specification, if clean, is classified as Buna S.V. All scrap is classified as Buna S.A. (ausschutz). The latter is passed through a disintegrator where it is shredded, then washed, dried and packaged in crumb form. Buna S.V. and even S-3 also appears occasionally in crumb form.

Monomer Storage

Monomers are stored (as of September 9, 1944) in ten storage tanks located in the tank farm, one of which (No.8) was knocked out by a heavy bomb prior to September 9, 1944.

Tank No.1	recycled styrene	- 7,700 gals.
" " 2	reserve styrene tank	- 7,700 "
" " 3	pure styrene	- 7,700 "
" " 4	pure butadiene	- 11,000 "
" " 5	recycled butadiene	- 11,000 "
" " 6	hydrocarbon mixtures	- 11,000 "
" " 7	—" — "	- 11,000 "
" " 9	reserve for hydrocarbon mixtures	- 11,000 "
" " 10	reserve for recycled butadiene	- 11,000 "

The styrene storage tanks each have one inlet from the styrene recovery unit, one exit to the styrene pump, one float level indicator (which reads in cubic meters), thermometers for temperature control, inlets for nitrogen, vacuum, safety pressure release, and an immersed pipe for draining off water. Butadiene tanks are equipped similarly.

Although butadiene tanks are tested to 8 atmospheres pressure, operating pressure is held to 4.5 atmospheres. An "Askania" control, provided with a warning alarm, vents excessive pressure through an outlet over the roof of the building.

Monomer Mixture

Emulsification, polymerization and stripping operations take place in building Lu 193. This building is a high ceiling, single story, totally enclosed structure with balconies across the north and south ends.

Butadiene and styrene are piped directly from the manufacturing plants. A hydrocarbon mixture is made up from pure and recycled butadiene and pure and recycled styrene. The mixture, calculated on a 100% basis, is composed of 70/30 B/S by weight. The following quantities of monomers expressed on a pure basis ("Kg 100%") are representative of regular operations: 10,465 Kg as fresh butadiene, 5,635 Kg as recycled butadiene, 5,175 Kg as fresh styrene, and 1,725 Kg recycled styrene. Actual amounts of fresh and recycled monomers ("Kg eff.") are calculated on the basis of fresh butadiene as 98% (± 0.5%), recycled butadiene approximately 1% less, fresh styrene at 100% (actually mostly 99.5%), and recycled styrene as 95% purity. Styrene purity is checked weekly by refractometer, and fluctuates close to 95%. The blend weights or "Kg eff." are converted to volumes ("Liter"), using specific gravities of the individual components. This value is termed "Liter-Soll". From this quantity is deducted the amount of pure styrene required for the preparation of the 10% Diproxide solution. Assuming that 0.08% Diproxide calculated on the hydrocarbons is to be charged, this amounts to 185 liters of pure styrene.

The butadiene and styrene are mixed together outside of the building for not less than 1½ hours. The blend is then pumped by a centrifugal pump through a flow meter to a mixing tee where it meets a stream consisting of the emulsifying ingredients dissolved in water fed by a similar centrifugal pump.

Emulsifier Solution

Two heated, stirred 16,500 gallon tanks are located on the lower floor for emulsifier solution make-up. Condensate water is charged to the tank, followed by liquid or solid Nekal, caustic and fatty acid. The following recipe and procedure is used:

Condensate water	- 8,800 gallons.
Nekal	- 10% less than calculated
Condensate water	- to 12,760 gallons
After one hour's stirring	- refractometer test
If too little Nekal	- Nekal is added according to a curve
After another one hour's stirring	- refractometer test
NaOH and fatty acid added	
Filled up to 14,850 gals.	
After one hour's stirring	- final refractometer test

The strong foam formation makes it difficult to measure Nekal solutions. At Schkopau it was found that refractive index could be

used to control Nekal concentration. Using standard solutions, a diagram of refraction index vs. Kg of Nekal was prepared.

The solutions are heated to a definite temperature during make up and are held at that temperature. Temperature is difficult to maintain during cold weather because of outside storage.

Activator Solution

The 4½% activator solution is made up in a 990 gallon tank. In document 1814-16 it is stated that this tank is rubber-lined. Condensate water (880 gallons) and 163 Kg of $K_2S_2O_8$ are added, the charge being diluted to 946 gallons. After an hour's mixing a sample is taken. When the contents vary no more than ± 0.1%, the charge is run through a filter. If the solution is stored outside during the winter there is danger that the solution will crystallize out, causing the filters to clog. In this instance, pipes must then be warmed up with steam.

Diproxid Solution

In Document 1814-4d it is stated that for the preparing of Diproxid Solution, 700 Kg of pure styrene are introduced into a 220 gallon enamelled vessel equipped with an agitator. Ten grams of Diproxid per 100 cc of styrene are then added. To remove water 2 Kg of sodium sulfate are added. After one hour's stirring, the solution is drawn off over a cloth filter. It flows to a measuring vessel at the head of each row of reactors and runs into a standpipe which controls the feed.

Polymerization

In the center of building Lu 193, space is provided for six lines of reactors, eight to a row, set into the floor and projecting downwards into the basement. In July 1944, four rows were in operation, and a fifth row (from Italy) was also available. At the time of our visit, however, only three lines of eight reactors each were installed. The others had been shipped away, presumably to some other plant. Ingredients are charged to the reactor rows from pumping stations. These are composed of control apparatus, meters, agitators, and recorders for transferring and metering the blended hydrocarbons and the aqueous phase from make up tanks to the reactors. There are two parallel-operating pumping stations, one of which was to be held in reserve. There are four centrifugal pumps each one of which can serve all the rows of reactors. So many spare pumps were considered necessary because the complete production depends on their operation, and because it occasionally was necessary to manufacture two different products at the same time. Hydrocarbons and aqueous phases are emulsified in a mixing tee which follows the pumping equipment. The

quantity of aqueous phase fed to the emulsifying tee is automatically regulated by a flow controller at the make up tank. The proportion of hydrocarbon phase mixed with this emulsifier solution is controlled at the metering station preceding the Tee. Both hydrocarbon and water phases are metered by displacement instruments. Weight recorders are installed in both lines following the meters to maintain constant control in case the meters have to be by-passed. Auxiliary equipment includes pressure manometers and thermometers above and below the meters as well as two parallel operating filters in each line. These filters are rubber coated. Piping is arranged so that ethylbenzene can be used as a purge when the hydrocarbon mixture is not being charged.

The hydrocarbon meter is made of cast iron, and the emulsifier meter is made of metal "VA". Although the hydrocarbons as such are not corrosive, meter corrosion is frequently caused by traces of water and water flushing.

Normally the feed enters the first reactor through a delivery line extending to the bottom of the reactor. This reactor discharges from the top through a line to the bottom of the second reactor, and so on for all eight reactors. Reactors are operated full. The piping is so arranged that any reactor can be by-passed, and the contents of any reactor can be run directly to the discharge line. Normally only seven reactors in each line are in use, with the eighth out for cleaning or stand-by.

The rate of feed is controlled by a flow regulator of the diaphragm type to between 3000 and 4000 liters per hour. Capacity of the reactors is 20,700 liters each. Total reaction time was said to be 24 to 30 hours, but these figures would indicate a longer period. The water jacket temperature of the first reactor is hand controlled so that latex at exit reaches 50°C. The rest of the reactors are held at this temperature.

The progress of the polymerization is checked by sampling latex from the discharge line of each reactor and determining conversion from total solids. Hydrocarbon conversions should be between the following limits:

1st reactor	7 to 11% of total monomer
2nd "	15 to 20% " " "
3rd "	25 to 30% " " "
4th "	32 to 37% " " "
5th "	40 to 45% " " "
6th "	47 to 52% " " "
7th "	55 to 60% " " "

Total solids of later leaving the last reactor are 30 to 32% by weight.

The persulphate and di-isopropyl xanthogenate are added continuously in equal amounts to the second, fourth and sixth reactor by means of an adjustable stroke displacement pump. The presence of a calibrated measuring tank indicated that the metering pump was not always relied upon. Sufficient modifier (MEK) is used to allow the formation of such molecular linkage that the final Buna, after heat softening of 50 minutes, possesses a Defo value of 3200 on the average.

Agitation in the reactors was the simplest possible consisting of a vertical square shaft having four horizontal flat cross pieces fixed on it at regular intervals and extending to within a few inches of the reactor walls. The agitator was driven by an 8 kw motor to give a speed of 20-25 r.p.m.

All vessels for handling hydrocarbons and process water were stated to be V-A steel (believed to be a chrom-vanadium steel alloy). Pipes and fittings were said to be plain steel.

Reaction vessels were said by the plant manager to require cleaning every six months and lines only once a year.

In a discussion with Dr. Teupel at Ludwigshafen, Mr. Handley was given the following recipe:

	Parts by weight
Butadiene	70.0
Styrene	30.0
Nekal (sodium dibutyl naphthalene sulphonate)	3.0
Sodium paraffinate	0.5
Sodium hydroxide	0.4
Potassium persulfate	0.4
Di-isopropyl xanthogenate	.06 to .10
Treated water	106.00

Although no reference is made to di-isopropyl xanthogenate in Document 1814-4d, a procedure has been given for preparation of a styrene solution of Diproxid. It is not known at this time whether or not these two materials are the same.

Antioxidant and Shortstopping

A 20½% phenyl-beta-naphthylamine (PBN) dispersion containing

Nekal was added continuously to shortstop the reaction and to stabilize the finished Buna. A calculated amount of 3% PBN based on the rubber was added.

When ground PBN is used, 2000 Kg of PBN is added gradually to 1760 gallons of condensate water. Fifteen Kg of Nekal and 7.5 Kg of 100% NaOH are then added to improve the dispersion. The charge is then diluted to 2200 gallons. After four hours' agitation, a sample is taken, and correction is made according to the solids content. Foam formation makes it difficult to get an accurate solids determination. The contents of the vessel are agitated continuously to obviate settling.

It was reported that the PBN dispersion at Schkopau is prepared by melting the PBN in a 1100 gallon kettle heated with steam at three atmospheres. The melt is then transferred to a turbomixer where it is mixed with a dilute solution of emulsifier. It is then transferred to a 4400-gallon vessel equipped with an agitator. The dispersion is then piped through a colloid mill and run into another tank.

Recovery of Unreacted Monomers

The latex stripping and monomer recovery equipment is located at the north end of the building.

This part of the process is not well developed. 10% of the recoverable butadiene is said to be lost and 25% of the recoverable styrene. After stabilizing with phenyl beta naphthylamine (no hydroquinone is used) the latex is pumped directly to the top of a vacuum steam stripping tower without previously flashing the butadiene. It was stated that recovered monomers were blended with fresh stocks until the purity of the butadiene became less than 60%, after which it was returned for purification. No documentary evidence was found in support of this, but cost figures verify the recovery losses.

In Document 1814-16 reference is made to filtration of the latex-stabilizer mixture prior to stripping.

Coagulation

The stripped latex is pumped to blending tanks near building Lu 195 where the coagulation, filtration, drying and packaging operations take place. This is also a single storied structure with a balcony across the south end. Tanks for making up coagulants are located on this balcony. Four finishing lines, each consisting of a panel board for controlling the rate of flow of the latex, coagulents and dilution water, a fourdrinier, a dryer and an automatic roller-weigher

are arranged parallel to one another along the length of the building.

The stripped latex is pumped to two large tile-lined blending tanks of 150 cu.m. capacity located at the south end of building Lu 195. These tanks are fitted with propeller agitators.

A continuous two step coagulation is carried out without the use of tanks.

Latex flows from one of the blending tanks under gravity through a 3" pipe made of polyvinyl chloride. It is mounted on a control panel which is fitted for measuring rate of flow of latex and the two streams of flocculating and coagulating chemicals.

The first coagulent stream is injected into the center of the latex pipe at an elbow, through a nozzle designed to give it a spiral motion. The rate of flow at this point is:

Latex	2400	liters	per	minute
$CaCl_2$ 36% solution	250	"	"	"
NaCl saturated solution	1000	"	"	"
Water	3000	"	"	"

(These values appear to be inconsistent with reactor flows and will be rechecked)

About 15 ft. further along the latex pipe a coagulating stream consisting of 12 to 16,000 liters of water and 16 liters acetic acid is introduced through a second similar jet. A third jet is provided for the introduction of more water if required. Final pH is between 5 and 6. For each 100 kgs of rubber these quantities are required:

First stream	Calcium chloride	5.0 kgs
	Sodium "	10-20.0 "
	Water	1000 liters
Second stream	Acetic acid	1.0-1.5 kgs
	Water	4000 liters

The coagulated latex enters the bottom of a deep weir box and flows over a carefully designed weir on to a fine travelling screen about 2 meters wide on a fourdrinier-type paper machine. The total length of this continuous screen is 37 meters, so that its operating length supported over a drainage tank on hard rubber rollers is somewhat less than half that. It travels at 8 to 11 meters per minute. The filtrate runs to a settling basin for recovery of fines and is discarded.

A short distance before the rubber is removed from the screen a pressure roller having a fine wire mesh surface compacts the rubber

layer and a vacuum is applied beneath the screen for a distance of 24". The rubber blanket is picked off as the screen passes over a large terminal roller and is further compressed between a pair of ribbed hard rubber-covered rollers on which pressure can be carefully adjusted.

Drying

The blanket is then elevated by means of an inclined travelling belt to the top of a 19 pass dryer which is divided horizontally into four compartments, in each of which air is circulated by means of numerous fans. The temperature in the first or top compartment was maintained at 125°C by means of finned steam coils, in the second 115°C, the third 90 to 100°C and the fourth was at room temperature for cooling the rubber.

Finishing

The blanket leaving the dryer is slit down the middle and each half is rolled up to a measured weight on a take-off similar to a calender take-off, in rolls weighing about 50 kgs. These are packed in burlap bags.

Finished rubber is stored in adequate space remaining at the north end of the building.

Koresin is made at Ludwigshaven by reacting acetylene with para-isobutyl phenol. The latter is produced by a standard Friedel-Craft reaction between isobutylene of 95% purity obtained from the alcohol, and phenol as follows:

Isobutylene is introduced continuously into a porcelain-lined jacketed autoclave, fitted with a stirrer, and containing phenol. A temperature of 50°C and 5 atmospheres pressure is maintained. Anhydrous aluminium chloride and phenol are added continuously mole for mole. The product is withdrawn continuously from the bottom, is neutralized, washed and decanted continuously. The crude produce is batch distilled at atmospheric pressure. Phenol is recycled and the fraction distilling between 92 and 95°C is the paraisobutyl phenol of 95% purity used in the next step. Bottoms are discarded.

In the next step 800 kgs. isobutyl phenol and 70 kgs. zinc naphthenate are melted and mixed in a jacketed stirred kettle at 90°C and introduced under nitrogen pressure into a heavy horizontal cylindrical autoclave of 1.5 cu.m. capacity which has been previously purged with nitrogen. This autoclave is fitted with a stirrer consisting of a horizontal shaft rotating at 35 r.p.m. having a number of straight projecting arms. It is surrounded by a high pressure steam jacket.

The contents are heated to 180°C by 20 atmospheres steam pressure in the jacket and after discontinuing heating acetylene is introduced at a rate sufficient to increase the temperature to 230°C but not above 240°C. The reaction was said to proceed under 15 to 20 atmospheres pressure and it was not clear whether this pressure was obtained with nitrogen previously to introducing the acetylene or not.

Reaction time is 8 hours, total cycle 12 hours. Theoretical consumption of acetylene is 165 cu.m. but actual consumption as measured by the meter in the plant was usually 180 cu.m. Addition of too much acetylene prevents removal of the product from the autoclave. No means of cooling were provided.

Toward the end of the reaction samples of product are taken and melting point determined in a Ubbelohde instrument. When this reaches 135°C the product is discharged to an open stirred kettle to remove acetylene and nitrogen. This kettle and all pipes are steam jacketed. The product, Koresin, without further treatment is packaged hot in paper-lined plywood drums and allowed to cool and solidify. Specifications are by melting point which must be between 135°C and 150°C. Yield per batch 1020 to 1040 kgs.

A sample of the zinc naphthenate employed was obtained but since this was not made at Ludwigshaven but at the I.G. plant at Griesheim-am-Main no further information on it was available. The Ludwigshaven installation for production of Koresin located in building No.926 consisted originally of three autoclaves of the type described, but a bomb destroyed part of the equipment. Two are now capable of operating when services and acetylene supply are restored. Maximum capacity is stated to be 50 tons monthly per reactor. With a 12 hour cycle on continuous production it is obvious this equipment should be capable of slightly more output.

Isobutyl phenol is produced in building No.114 in equipment capable of much larger output than needed for Koresin. The excess is sold to resin manufacturers for condensation with formaldehyde.

Koresin was first produced in 1940 or 1941 in one autoclave at the rate of 30 to 40 tons per month. This was gradually increased to 100 tons per month average production during 1943. Bombing in about October 1944 knocked out two autoclaves one of which was restored to operation by December. Nevertheless the plant operators stated that total production since October has been about 100 tons due to a continuous series of interruptions in supplies or services.

So far as the personnel interviewed know, no information concerning Koresin has been furnished to the Japanese.

Personnel interviewed on Koresin:

Dr. Wolgang Bulow.	Director of Solvents and Plastics Div.
Dr. Ernst Keyssner.	Manager of Koresin Plant.
Dr. Karl Pflaumer.	Director of Intermediate Chemicals (Isobutyl phenol)

Koresin Compressor and Autoclave

Dr. Hopf of the Ludwigshafen research laboratories had the following to say about Igamid:

The types made are:

Igamid A - Nylon duplicate.

Igamid B - A nylon type material made from Amino-caproic acid.

Igamid BS - A lower molecular weight B developed for tire cord.

Igamid CA - A mixture of Igamid A and B inter-polymerized. Soluble in alcohols.

The production capacity at Ludwigshafen is 200 tons per month of B or BS and 50 tons per month of A or CA.

There are no other plants producing Igamid in Germany.

The development of Igamid BS was within the last 18 months as it was developed after an investigation of American airplane tires showed nylon was being used.

Dr. Hopf claims his raw material Igamid "B" special gives a cord of better properties than Nylon. He claims the fibre is made in Berlin and twisted at Chemnitz.

The Igamid factory was destroyed by a direct bomb hit followed by a solvent fire. The machinery and equipment however, may be partially salvaged.

The adjoining research laboratory containing pilot plant equipment, however, is in good condition.

Document 1814-19, entitled "Research in Acetylene Chemistry at Ludwigshafen" by Dr. Reppe dated July 26, 1940 is a general review of the progress made in acetylene chemistry. This document should be studied in detail as a fundamental paper on new organic syntheses but a brief outline of this paper appears warranted here.

In brief Dr. Reppe points out that vinylation is now a recognised reaction similar to nitration, sulfonation, etc. Various vinyl compounds may now be synthesized such as:

(a) Vinylethers for resins, adhesive, leather, textile finishes and pour point depressants and rubber softeners.

(b) Polyoxystyrenes for rubber tackifiers (Koresin, etc.)

(c) Vinylesters for drying oil substitutes.

(d) Vinyl sulfides - no use yet developed.

(e) Vinyl amines.

(f) Ethenyl compounds such as propargylamines and amino-butines.

(g) Alkinols - particularly butindiol for butadiene syntheses and the preparation of substitute butadienes.

The syntheses of such important materials as adipic acid, maleic acid, maleic anhydride, polyamids, etc., are discussed in this paper. Other items of interest are allyl alcohol, carboxylic acids, glycerine and many types of plastics.

APPENDIX

SUMMARY OF DOCUMENTS OBTAINED ON LUDWIGSHAFEN TRIP

NO.	CONTENTS
1814-1	Daily Buna production and inventory from start of operations 10/3/42 to 15/12/44. This shows main use of chemicals in buna finishing and production by finishing machines.
1814-2	Text Book "Kunststoffe im technischen Korrosionsschutz Handbuch fur Vinidur und Oppanol" by Walter Krannich (J.F. Lehmanns Verlag 1943). This is a general handbook on polyvinyl chloride and polyisobutylene polymers.
1814-3	"Bunaprufstelle" 7 November 1940 to 23 May 1942. Miscellaneous test data comparing production Buna from Schkopau, Ludwigshafen and Huls. Also comments on a few experimental batches. A description is given of the method of obtaining deformation tests.
1814-4a	File entitled "Buna-lager, Produktions-Absatz-u Bestandsmeldung". This is a monthly summary of buna production by types and quantities as well as shipments from the start of operations to March 1945.
1814-4b	This contains a file of instructions for shutting down various operations in case of air raid alarms. Included are shut-down procedures for the acetylene, butandiol, butindiol and furan plants. Some description of an acetylene explosion is given. Fragmentary data show the influence of shut-downs due to raid alarms on production of butandiol(?).
1814-4c	13 May 1943 to 12 August, 1944. Discussions of staff personnel problems.

NO.	CONTENTS
1814-4d	'Der Chemisch-Technische und Wirtschaftliche Stand des Buna-1, 4-Verfahrens Ende 1944" by Dr. Schor - Ludwigshafen 31.1.45. Manufacturing costs at Ludwigshafen are compared with those at Schkopau. A table is given for anticipated over-all efficiencies on raw materials. An outline is proposed for the compilation of data related to Buna production so that a handbook can be prepared. Certain steps in the Buna polymerization plant are described in detail on handwritten sheets, apparently the first step towards the preparation of the handbook.
1814-5	File entitled Direktionsabteilung covering requests and allotments for chemicals for Buna production.
1814-6	a. Report on the use of control and measuring instruments at Schkopau by Dr. Walker Nov. 12, 1940. b. Report on Butadiene distillation in Schkopau by Dr. Broich Nov. 12, 1940. c. Report on Butol distillation in Schkopau by Dr. Strobele Nov. 12, 1940. d. Report on Ethylbenzene distillation in Schkopau by Dr. Winkeler Nov. 12, 1940. e. Report on Styrene distillation in Schkopau by Dr. Winkeler, Nov. 12, 1940.
1814-7	Report from Oppau on the infared spectra of high polymers especially by butadiene polymerization by Dr. Karl Luft, April 1944.
1814-8	A large aerial photograph (from near ground level) of entire Auschwitz plant showing all important buildings, which are marked as to their utility.
1814-9	Photographs of Italian Rubber plant at Ferrara.
1814-10	A schematic flow sheet of a pilot plant for the catalytic dehydrogenation of Ethylbenzene to Styrene using oxide catalyst with steam addition.

NO.	CONTENTS
1814-11	A map found in Dr. Ambros' file showing location and monthly production capacities of acetaldehyde and buna at each plant. Indication of underground storage of acetaldehyde in south Germany and perhaps underground plant for buna production in south Germany near Nurmberg.
1814-12	This is a general emergency rubber program for Germany dated November 1942, with indications of anticipated productions at each plant and monthly comments during 1943 on the actual performance.
1814-13	A booklet entitled "Taschenbuch fur die Gummi-Industrie". This is a general rubber handbook.
1814-14	Report on the costs and yields of the various products made at Schkopau for the fourth quarter of 1943. Summary costs for the remaining quartersare also shown.
1814-15	Set of monthly summary reports for July 1944 to March 1945, on each step of the buna process. These show inputs, yields, catalyst performance, air raid effects, labor usage, etc.
1814-16	"Betriebsbeschriebungen" 28 January 1942 to 6 November 1943, by Teupel and Niemann. General discussion of the flow of material in butadiene and Buna manufacture with miscellaneous comments on butadiene and styrene storage.
1814-17	A summary of a material balance on the Ludwigshafen carbide plant for the first eight months of 1944.
1814-18	Report on the use of residues from 1.4 butandiol distillation by Drs. Krzikalla and Fleckinger November 30, 1944.
1814-19	A report dated July 26, 1940 by Dr. Reppe on the general use of acetylene in the production of many compounds. Basic organic chemical research report on the Reppe butadiene process. Koresin, vinyl ethers, alkinols, adipic acid, maleic acid, etc.

NO.	CONTENTS
1814-20	A report by Dr. Niemann, Jan. 24, 1941, relating to pilot plant results on the various steps of the Reppe butadiene synthesis. Time, temperature, catalyst, yields, etc., are all covered quite thoroughly.
1814-21	Report on the use of butadiene distillation residues by the Reppe synthesis by Drs. Krzikalla, Dornheim and Fleckinger, Sept. 14, 1944.
1814-22	Report on by-products of butindiol hydrogenation by the Reppe process by Dr. Jutz, Nov. 11, 1944.
1814-23	A report by Dr. Niemann dated May 12, 1944, on the butadiene plant at Ludwigshafen presented before the inorganic colloquium. This is the most recent and complete report on the Ludwigshafen process.
1814-24	Report by Dr. Reppe dated July 25, 1940, relating to the specific application of the general Reppe syntheses to the manufacture of butadiene.
1814-25	File of three sections on "Prufberichte" showing test results on Buna M, Buna Disk, Buna S and Miscellaneous.
1814-26	File of correspondence from Oppau Ammoniak laboratory dealing mostly with special polymers such as mixed isoprene polymers with dimol and acrylo nitrile. Many chemical problems are discussed, including butane dehydrogenation over chrome-alumina catalyst. Discussion of pharmaceuticals research. A review of the general German Chemical Industry from 1910-1935.
1814-27	A memorandum from Huls dated Nov. 17, 1943, on the procedure for filling and unloading butadiene tank cars.
1814-28	"Herausnehmen eines Polymerisations - Kessels" by Dr. Teupel - Ludwigshafen, 26 October, 1943. Describes method of cutting a reactor off the line.
1814-29	a. Literature review of the manufacture of butadiene from ethylene and acetylene by Dr. Schmabel, Oct. 29, 1938.

NO.	CONTENTS
1814-29	b. A description is given for pilot plant preparation of Bunol which is apparently an oxidized low molecular weight polymer of butadiene. Polymerization is catalyzed with a sodium-potassium alloy. The oily product is neutralized and then blown with air to give the desired properties.
1814-30	July 1939 to February 1945. Miscellaneous comments on application of various Buna rubbers in consumers goods. Contains numerous compounding formulae.
1814-31	A file on Igelit showing various samples of compounded Igelit and their composition.
1814-32	A plan of the Ludwigshafen plant.

LIST OF DOCUMENTS MICROFILMED

SHAEF Reference No.	SHAEF Reference No.
1814-4a	1814-10
1814-6a	1814-12
1814-6b	1814-14
1814-6c	1814-19
1814-6d	1814-20
1814-6e	1814-23
1814-7	1814-24