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The Joint Chiefs of Staff,
by Col. E. W. Gruhn.

RESTRICTED

THE LEVERKUSEN WORKS OF I.G. FARBEN

Handley

RESTRICTED

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE

RESTRICTED

THE LEVERKUSEN WORKS OF I. G. FARBEN
LEVERKUSEN

Reported By _____

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CIOS Target Number 22/2

Miscellaneous Chemicals

[1945?]

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

RESTRICTED

50p.

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TARGET

The Leverkusen Works of I. G. Farben CLOS Black List Target 22/2.

TEAM

Leader - E. T. Handley	U. S. Civilian
Robert Juve	U. S. Civilian
B. S. Garvey	U. S. Civilian
N. R. Rowzee	Canadian Civilian

ITINERARY OF TEAM

The team was notified on April 23 by Major Hardiman the CAFT leader that the target was ready for investigation. The team was part of the team that had just finished investigating the synthetic plant at Huls which is located less than 75 miles from Leverkusen. The team proceeded to Leverkusen on the morning of April 24 arriving there around noon. The investigation required two and one-half days and the team started back to Paris on the evening of April 26. They arrived in London on April 30 after a stop-over in Paris waiting for transportation.

PLANT PERSONNEL

The team was only interested in the Central Research Laboratory and Buna "N" production items of the I.G. Leverkusen plant and found the key personnel of their departments on hand and cooperative. Dr. Konrad, the General Manager, Dr. Stocklin, the Technical Service Manager, were most helpful.

DOCUMENTS

No papers or documents had apparently been removed from the plant but most of the records were stored in the basement to protect them from bombing. Two bags of documents were selected and sent back to London to be studied and the more important ones will be recorded on micro film for future reference. A list of the documents removed is attached to this report.

In addition to the above mentioned documents the

team brought back with them specially prepared reports made by Dr. Konrad and members of his organization. A list of these appears as exhibits in the preliminary report dated May 2, 1945, copy of which is attached.

GENERAL DESCRIPTION OF THE PLANT

The Central Research Laboratory for Rubber (Target 22/2) was completed in 1939 at a cost of 10,000,000 Marks. It is probably the largest, best equipped and most modern plant of its kind in the world.

In addition to having pilot plant facilities for making synthetic rubbers, extensive physical and chemical laboratories, and technical service laboratories, it has facilities for building tires, tubes, hose and boots, and shoes; also testing equipment for evaluating these finished products.

The annual budget for operation was around 4,000,000 Marks. Exhibit #2 appended to our preliminary report dated May 2, 1945, gives the floor plans of the plant and Exhibit #1 gives the names of the thirty-five doctors employed. In addition some five hundred people were required to staff the plant.

The Leverkusen plant of I.G. Farben in addition to being the location of Central Research Laboratory for Rubber, which was our target, made many other chemical products. Some of the products made at the Leverkusen plant were: lithopone, titanium dioxide, fluorides, active charcoal, guanidine nitrate.

Benzol, toluol, nitrobenzol, dinitrobenzol, nitro-naphthalene, diamino toluene, chlor benzene, phenol, salicylic acid.

Acrylonitrile, synthetic oils, anthroquinone, dyestuff, intermediates, pharmaceuticals (acetanilide, atebtrin, sulphonamide, elladione), DDT (100 tons per month), photographic paper.

While other parts of the works at Leverkusen had been badly damaged by bombs and shell fire, the Rubber Research Laboratory had suffered only broken windows and minor equipment damage.

The various members of the team investigated various phases of the Leverkusen plant and their reports are attached.

E. T. Handley

LIST OF DOCUMENTS OBTAINED AT LEVERKUSEN

1. Handbook - Gummi Industry
2. Folder - Kautchuckindustrie
3. Folder - Track Block Tests
4. Envelope of Photos
5. Folder - Pruf and Arbeitvorschriften
6. 2 Folders - Erfarungs - Austausch
7. Envelope of Research Reports of Doctors - Blomer, Bachle, Stocklin, Noch, Fromandi, Demstedt
8. Envelope of Research Reports of Doctors - Wolz, Ecker, Becker
9. Envelope of Research Reports of Doctors - Konrad and Meisenberg
10. Envelope of Research Reports of Doctors - Sinn, Rohm, Rathjen, Muhlbausen, Garten, Logeman, Graulich
11. Envelope of Technical Committee Meeting Reports
12. File of Reports of Various Authors
13. File on Igetex
14. File on Regenerat
15. File on Weichmacher

A study of a report of Dr. Konrad's dated January 3, 1944, discloses some interesting information on the consumption of the various rubbers from 1938 through 1943. A summary of this information will be found below:

A

CONSUMPTION OF CRUDE RUBBER
RECLAIM AND BUNA IN GERMANY
IN 1,000 TONS

	<u>1938</u>	<u>1939</u>	<u>1940</u>	<u>1941</u>	<u>1942</u>	<u>1943</u>
Crude	97.0	61.0	27.0	22.0	26.5	4
Reclaim	29.0	34.0	46.0	46.0	40.0	50
Buna	<u>5.0</u>	<u>14.0</u>	<u>40.5</u>	<u>51.5</u>	<u>70.0</u>	<u>90</u>
Total	131.0	109.0	113.5	129.5	136.5	144.0

AVERAGE MONTHLY CONSUMPTION
IN 1943 OF RUBBERS WAS 11,500 TONS
THIS 11,500 TONS WAS CONSUMED IN
THE FOLLOWING END PRODUCTS

<u>TIRES</u>	<u>TONS</u>	6100
Bicycle tires and tubes	320	
Motorcycle tires	45	
Passenger tires	230	
Small truck tires	305	
Truck and bus tires	3,025	
Truck tubes	370	
Airplane tires	260	
Airplane tubes	50	
Bogies and track blocks	1,025	
Giant tires	55	
Airbags	40	
Repair materials and camelback	390	
<u>TECHNICAL GOODS</u>		5400
Dip goods	830	
Hose	420	
Jar rings - bottle caps	120	
Industrial boots - Overshoes	380	

TECHNICAL GOODS - (Continued)

TONS

Soles and heels	1,120
Surgical goods	135
Coated fabrics	160
Wire and cable	670
Hard rubber products	350
TOTAL	11.500

RUBBER LABORATORY AT LEVERKUSEN

Leverkusen as headquarters of the I.G. Farben research and development program on synthetic rubber had an exceptionally fine laboratory devoted exclusively to synthetic rubber work. This laboratory was considerably larger than those recently built by Goodyear and Firestone in Akron.

The laboratory at Leverkusen consisted of a large U-shaped building with a basement, ground floor and four upper stories. It was completed in 1939 at a cost of nine to ten million marks. The director of the synthetic rubber part of the I.G. Farben Works at Leverkusen was Dr. E. Konrad who stated that the annual operating budget was four million marks. It was by far the most complete and finest synthetic rubber laboratory the writer has seen.

The total personnel required to operate the laboratory was approximately 500. There were about 35 doctors who directed the work and carried out the major research projects. There were approximately 150 trained technical personnel and the remainder were ordinary workmen.

The key personnel under Dr. Konrad were

Dr. W. Becker	- Director - Chemical Development Dept.
Dr. Stöcklin	- Director - Technical Service.
Dr. Ecker	- Technical Service - Testing.
Dr. Bächle	- " " - Latex and Fabric.
Dr. Pohle	- " " - Fillers, Accelerators, and Antioxidants.
Dr. Loblein	- Director - Technical Service on Special Products.
Dr. Gartner	- Director - Compounding.
Dr. Oettner	- Director - Tire Building & End products.
Dr. Roelig	- Director - Synthetic Rubber Utilization.

In the basement of the laboratory building were a coating and spreading room, weighing room for experimental rubber laboratory, air raid shelters, and general storage space.

On the ground floor was the experimental rubber laboratory where there was a complete setup for mixing,

compounding, calendaring, extruding tubes and treads, dipping of fabric, building of tires, curing of tires and tubes, heat treatment of synthetic rubber, and the necessary control laboratories.

The mezzanine floor was split between the experimental rubber laboratory and laboratories devoted to testing connected with the technical utilization of synthetic rubber. The former consisted of equipment for the fabrication of wire and cable products, rubber footwear, hose, rubber belting and other mechanical goods especially surgical. The latter consisted of large rooms for dynamic testing and electrical testing and a small room for high potential electrical testing.

The first floor was devoted entirely to the testing and customer service department. Some of the principal sections were a room for the mixing and preparation of white and colored stocks, a similar room for black mixing, a calender room, a section of vulcanizing presses, vessels for steam curing, vessels for thermal softening of synthetic, equipment for preparing cements, spreading cements, dipping and drying of fabrics, a laboratory for optical work, a laboratory for testing of compounding ingredients, a very complete laboratory for compounding and testing rubber, a reception room, a laboratory for the technical men handling customer service, and offices for the same men.

It was learned that for service purposes Germany and Occupied Europe were divided into specific areas. The technical service men responsible for these areas each had offices in the customer service section of the laboratory building. Complaints and requests for information and assistance were handled by these men who were responsible for seeing that the necessary laboratory work was started promptly. The results of such work was transmitted to the users of the rubber by the men responsible for the various areas. The customer service men were held responsible for the proper utilization of rubber and dissemination of information in the various areas.

The second floor of the laboratory building consisted of general chemical research laboratories, general testing and development laboratories, executive offices, and library. The principal laboratories were a laboratory for physical chemical measurements, glassblowing room, general organic and physical chemical laboratories, a textile laboratory, a latex laboratory, and a well equipped pilot plant.

~~The pilot plant was felt to be of particular interest. Following is a reasonably complete list of its equipment:-~~

16 - 20 liter reactors - jacketed
12 - 50 " " "
4 - 150 " " "
2 - 500 " " "

Most of the above were stainless steel or chrome plated; all had variable speed pulley drives.

- 1 - Continuous tube reactor (described in detail in separate section)
- 3 - bottle polymerizers with space for 100 bottles each.

It was estimated that they were for bottles up to 16 oz. Each bottle fits into a perforated metal container which served as a shield in case of breakage. The bottles were rotated in an air bath. Each unit was equipped with a variable speed drive.

- 1 - bottle polymerizer for larger bottles of approximately 1 liter capacity.
- 2 - large tray driers - heated by circulating hot air from steam coils.
- 1 - small tray drier - heated by circulating hot air from steam coils.
- 1 - small vacuum drying oven.
- 1 - 6 x 12 mill.
- 1 - 6 x 12 washing mill.
- 1 - Laboratory model fourdriniere.

Miscellaneous small stills.

A room designed especially for high pressure polymerization.

Miscellaneous glass lined and earthenware vessels for coagulation.

The third floor of the laboratory building consisted entirely of storage space and locker rooms, washrooms, restrooms, and lunchrooms for men and women.

CONTINUOUS TUBE POLYMERIZATION AT LEVERKUSEN

In the pilot plant of the Leverkusen synthetic rubber laboratory was a continuous tube polymerizer in which it was claimed that reactions had been carried out to 60% in as little as 15 minutes.

The writeup obtained at Leverkusen stated that for proper polymerization in the continuous tube reactor, the flow rate had to be rapid otherwise separation occurred and the polymerization did not proceed smoothly. A long polymerization time required a proportionally long reactor. Continuous tube reactions at the normal Buna S reaction times were felt to be technically unsound. On this basis fast reaction mixtures were studied. Two methods of obtaining rapid reactions were found. They were the use of higher emulsifier concentrations and the use of a combination of oxidizing and reducing catalysts.

The physical setup of the continuous tube system was as follows. The letters used apply to the schematic diagram obtained at Leverkusen.

- A & B. Two 150 l. mixing vessels used for the makeup and feed of the essential ingredients to the continuous tube reactor. In one, a hydrocarbon mixture in the proper proportions was prepared; in the other, the emulsifier solution plus any other desirable water soluble ingredients was made up. These vessels were jacketed and equipped with variable speed agitation. They had the normal complement of valves. Each had a dip leg and a sight glass.
- C. Two metering pumps, one for the hydrocarbon mixture and one for the water soluble phase.
- D. A chromeplated premixer equipped with high speed agitation. It had a capacity of 20 l. and was equipped with the usual valves, a dip leg, and a sight glass.
- F. Safety gauge which registered pressure and shut off pump motors if pressure rose to abnormal levels.

- G. Reactor made up of 16 V₂A tubes 2.5 m. in length and having an inside diameter of 25 mm. The tubes were connected in series coupled with elbows and were slightly inclined in lattice form, number one tube being at the top of the framework. The total length was 44 m., total volume 22 l. The tubes were jacketed for purposes of heating or cooling. There were four separate sources of heating or cooling water. At the time of our visit the water was added at tubes Nos. 1, 5, 9 & 13 and exhausted from tubes Nos. 4, 8, 12 & 16. The setup was very flexible and was so arranged that water could be added to or exhausted from any tube within the limitations imposed by four sources of water. The reactor was equipped with four proportioning pumps which were used for addition of catalyst, antioxidant, and other ingredients as needed. These pumps had micro-meter settings and feed rates of 0 - 5 l. per hr.

The procedure followed in operating the continuous tube reactor was to make up the hydrocarbon mixture and the emulsifier solution in the 150 l. vessels. The flow from these two vessels was controlled by metering pumps and in the premixer the two streams were well emulsified. It should be noted that prior to use the entire system was swept to nitrogen and during use it was kept under nitrogen pressure. The emulsion on leaving the premixer flowed to tube number one of the reactor where it was heated to the desired temperature and maintained as close to that temperature as hand control permitted. The latex was discharged from the reactor thru control valves. The antioxidant PBNA was added by proportioning pump and the latex flowed to a vessel under a fume hood. The writeup and diagram made no mention of stripping the latex of residual butadiene and styrene. This was usually done in a batch still in the laboratory. The latex was coagulated with salt and acid. Catalyst was added in any one of several places; in the 150 l. containing the water soluble phase, in the premixer, in the line leading from the premixer to the first reaction tube, or in one or more of the reaction tubes.

In the operation of the continuous tube reactor, there was no agitation in the tubes. Baffles had been tried but they were removed when it was found they caused pre-coagulation. It was stated that the tube reactor had been run as long as 14 days without shutdown. The deposit of coagulum on the tubes after that period was not serious and was easily removed using a brush dipped in solvent. It was felt that

~~a straight tube of equivalent length would be preferable to several short lengths in series particularly from the standpoint of short circuiting and coagulum buildup on the tubes.~~

It was felt that the temperature control of the reaction was not of the best. Automatic temperature control was needed and possibly separate temperature control over the jacket water for each tube. It was stated that ~~e~~ experimentation with the continuous tube reaction had not been tried in a setup larger than the one described above and that work on it was still in the early stages.

Typical formulas and results follow:-

Formula No. 1

75	Butadiene
20	Styrene
<hr/>	
5	Nitrile
6	Nekal
2	Paraffin fatty acid
180	Water
	0.5 Ammonium persulfate
	0.66 Sodium hydroxide

Temperature of Reaction.	Conversion.	Time.
70° C.	60%	60 min.
50° C.	60%	4 - 5 hrs.

Formula No. 2

75	Butadiene
25	Styrene
4.5	Mersolat (C ₁₂ H ₂₅ SO ₃ Na)
144	Water
	0.5 Sodium pyrophosphate
	0.25 Sec. potassium phosphate
	0.25 Potassium ferrocyanide
	0.05 Ammonium persulfate

At 70°C., a conversion to 60% was obtained in 30 minutes.

It was stated that the rubber produced in the continuous tube at 70°C. was inferior to the normal Buna S but that that produced at 50°C. was equal to the standard.

It was mentioned that reactions had been carried out in as little as 15 min. at 50°C. using the combination oxidizing and reducing catalyst with the introduction of a feature the exact limitations of which had not yet been determined. The feature was the boiling of the water used in the reaction to expel Oxygen. It was claimed that the secret of ultra-fast reactions was found in the use of water having a very low Oxygen content. Experimental work had established that high oxygen concentrations in the reaction mixture and no oxygen whatever resulted in very slow reactions. It was admitted that optimum oxygen concentration in the reaction mixture had not been determined as yet. It was because of the critical nature of the oxygen concentration that the entire system was swept with nitrogen before use.

FORMULAS AND OTHER DATA FOR BUNA N RUBBERS PRODUCED AT LEVERKUSEN

	Buna N Perbunan	Buna NN Perbunan Extra	Igetex NN latex
Butadiene	74	60	60
Styrene <i>Acrylo</i>	26	40	40
Water	150	200	57
Potassium persulfate	0.20	0.20	0.50
Diproxid	0.50	0.27	0.27
(Diisopropyl xanthogen disulfide)	3.60	3.60	
Nekal			
Meprasin	0.30	0.30	3.75
Na ₄ P ₂ O ₇	0.05-0.10	0.10	0.30
NaOH	3.0% PBNA	3.0% PBNA	0.10
Antioxidant			1% HQ 2% Oxy-
Reaction Temp. °C.	30	24	Cresyl-camphon 25
Reaction time -hrs.	25-30	60	30
Type of Reaction	Continuous	Batch	Batch
Conversion -%	75	75 ?	62-65
Nitrile in polymer -%	26	36	-

PRODUCTION OF BUNA N-TYPE RUBBER AT LEVERKUSEN
IN METRIC TONS

	Perbunan	Perbunan latex	Perbunan Extra
1939	960	97	69
1940	1692	114	92
1941	2433	72	136
1942	2535	49	230
1943	3341	93	222
1944	2802	93	234

Igetex NN was produced at the rate of only one to two tons per month.

Perbunan Manufacture

Information contained herein was obtained from Dr. Holzrichter who was in charge of Perbunan production at Leverkusen.

Types:

Four types of Buna N rubber were prepared at Leverkusen:

Perbunan - regular solvent resistant rubber for fuel cells etc.

Perbunan sp. - regular Perbunan latex used for fabric impregnation, etc.

Perbunan extra - greater solvent resistance than regular Perbunan by virtue of higher acrylonitrile content.

Igatex NN - latex of 45% solids, used for high film strength dipped goods.

Buildings:

Polymerization and stripping operations occur in one building, and the latex is pumped to an adjacent building for coagulation, washing, and drying. The buildings are both quite large because other speciality types of Buna S are made in the same buildings. The old reactors used during the last war for Methyl Rubber are also located in the polymerization building. These old reactors have been used recently in making a Thiokol-type polymer and in making plasticizers, etc.

The plant contains two 10 cubic meter reactors and two 20 cubic meter blown-down tanks for pilot-plant work as well as 8 reactors of 20 cubic meters and 3 blown-down tanks of 30 cubic meters which are used for miscellaneous reactions.

The other building contains two fourdriniers 1 meter wide and one fourdrinier 2 meters wide, each being followed by driers. In addition, an old drier is present which is used for experimental batches.

The total employment in the two buildings is as follows:-

Polymerization:	3 Meisters
	30 workmen
Coagulation, etc:	2 Meisters
	25 workmen

Perbunan Manufacture:

Perbunan is polymerized continuously by preblending butadiene and acrylonitrile in two 20 cubic meter tanks and preparing emulsifier solution in two 15 cubic meter tanks and running the two phases together in a turbo mixer at the head of the line of reactors. All butadiene is obtained from Hüls. Part of the acrylonitrile comes from Ludwigshafen; the remainder is made at Leverkusen. The charging of the mixed monomers is controlled by taking hourly readings on the sight glasses on the preblend tanks and making appropriate adjustments on the piston pump which feeds to the turbo mixer. The emulsifier solution, containing Nekal, $\text{Na}_2\text{P}_2\text{O}_7$, and NaOH is fed similarly to the turbo mixer.

$\text{K}_2\text{S}_2\text{O}_8$ is dissolved in water in a 3 cubic meter rubber-lined tank. A small piston pump feeds the $\text{K}_2\text{S}_2\text{O}_8$ solution into the emulsified water-monomer line as it comes out of the turbo mixer.

The line of reactors consists of 6 vessels of 10 cubic meter capacity, made of V₂A metal. Only 5 of the vessels are used at a time, the 6th being down for cleaning or repairs. Diproxid dissolved in acrylonitrile is added in three equal parts to the latex at 0, 20, and 45% conversion by means of piston pumps checked with sight glasses on the Diproxid holding tanks. With normal reaction rate, the Diproxid is added to the first, second and fourth reactors, but occasionally it is added to the first, third and fourth.

The reactors are completely filled with latex during operation. Each reactor has an independent cooling water system. The reactor agitation is supplied by seven flat paddles mounted on the shaft alternately at right angles to each other. The shaft rotates at approximately 35 RPM. Reactors are operated for approximately two months without cleaning.

At the discharge from the last reactor the latex is at 75% conversion. After the latex has gone through a filter, a suspension of phenyl-beta-naphthylamine (PBN) is fed into the latex line continuously. The PBN is in a 12% dispersion, stabilized with Nekal. Three percent PBN, on dry rubber basis, is added.

Following the PBN addition, the latex is stripped of unreacted monomers by means of a vacuum distillation with steam. Recovered butadiene is compressed, cooled, and returned to a storage tank, to be reused. A separation of acrylonitrile and water is accomplished by fractionation. The final recovered acrylonitrile, containing 4-5% of water, is reused in batch reactions of Perbunan Extra. Of the unreacted monomers it was claimed that 90% of the butadiene and 50% of the acrylonitrile were recovered.

The degassed latex is transferred to a 40 cubic meter holding tank by means of a centrifugal pump. From the holding tank it is piped to the adjacent building where coagulation is accomplished with a 25% NaCl solution (150 kg of NaCl solution per 100 kg dry polymer) in a glass tube of the same type used for Buna S coagulation. Later flow is regulated with a monometer and coagulant flow is checked with a rotometer. The particle size is carefully controlled so that a uniform band is formed on the fourdrinier machine. The band is washed on the fourdrinier and the water content is then reduced to approximately 50% before it is introduced into the drier. The drier is a typical continuous circulating air oven which contains 17 passes. In the first zone the temperature is 125°C and gradually lowers until, finally, it is approximately 90°C in the last zone. The band coming out of the drier is powdered with talcum and wound into 100 kg rolls for shipment to consumers.

The polymerization recipe is as follows:-

			<u>Parts by weight</u>
Butadiene	74
Acrylonitrile	26
Condensate water	150
*Nekal BX	3.6 (calculated on basis of 100% solids)
$\text{Na}_4\text{P}_2\text{O}_7$	0.3
NaOH	0.05 to 0.1
$\text{K}_2\text{S}_2\text{O}_8$	0.2
**Diproxid	0.3

The overall reaction time amounts to 25-30 hours. The resulting product has a Defo value of 2400-2800, and the nitrogen analysis varies from 6.2 to 6.5%.

*Nekal BX contains 70% solids.

**Diisopropyl Xanthogen disulfide.

Manufacture of Perbunan Extra

Perbunan Extra is made by batch-wise polymerization in a 20 cubic meter reactor.

The polymerization formula follows:-

			<u>Parts by weight</u>
Butadiene	60
Acrylonitrile	40
Condensate water	200
*Nekal BX	3.6 (calculated on basis of 100% solids)
$\text{Na}_4\text{P}_2\text{O}_7$	0.3
NaOH	0.1
$\text{K}_2\text{S}_2\text{O}_8$	0.2
Diproxid	0.27

The reaction requires 60 hours at 24°C, the lower temperature being necessary because of the heat transfer problems in the large reactor.

The latex is transferred to a 30 cubic meter blown-down tank where 3% PBN is added. Coagulation is the same as used for regular Perbunan.

The product contains 36% acrylonitrile by analysis.

Preparation of Igatex NN

In the manufacture of Igatex NN latex, temperature control is difficult. At 5 to 7% conversion the reaction starts off very

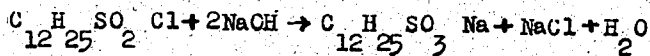
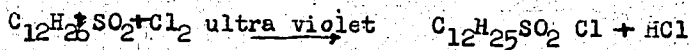
*Nekal contains 70% solids.

fast. Polymerization is conducted batch-wise, in 10 cubic meter reactors, according to the following recipe:-

		<u>Parts by Weight</u>
Butadiene	..	65
Acrylonitrile	..	35
Condensate water		57
*Mepasinsulfonate		3.75
Na ₂ P ₂ O ₇	..	0.03
K ₂ S ₂ O ₈	..	0.05
Diproxid -	..	0.39

The reaction is carried to 05% conversion at 25°C in approximately 30 hours. As stopping agent and antioxidant, 1% hydroquinone and 2% oxyeresyl camphan are added. After stripping of unreacted monomers the latex has a solids content of 45%. The product contains 36% acrylonitrile.

* Stated to be made as follows:-



Production Data - Tons Produced

	<u>1939</u>	<u>1940</u>	<u>1941</u>	<u>1942</u>	<u>1943</u>	<u>1944 (to 26 Oct.)</u>
Perbunan	960	1692	2433	2535	3341	2802
Perbunan Sp. (on dry basis)	97	114	72	49	93	93
Perbunan Extra	69	92	136	230	222	234

Igatex NN was made spasmodically at rate of 1 or 2 tons of latex per month.

100 cubic meters of Perbunan latex which has been made since 26 October, 1944 is now in the plant at Leverkusen.

Cost Calculations

(Based on butadiene and acrylonitrile costs in the second quarter of 1944)

<u>Perbunan Latex</u>	<u>Parts per 100 parts Polymer</u>	<u>Cost of the Outgoing Product</u>	<u>Marks per 100 kg. Polymer</u>
Butadiene	80.2	221.50	177.60
Acrylonitrile from Ludwigshafen	13.4	292.20	39.13
Acrylonitrile from Leverkusen	17.7	302.60	53.66
PBN	2.8	115.15	3.26
Nekal BXG	4.2	82.45	3.46
Nekal BX (dry)	2.6	68.15	1.77
Diproxid (pure)	0.4	321.85	1.28
Na ₂ P ₂ O ₇	0.3	88.50	0.23
K ₂ S ₂ O ₈	0.3	67.50	0.21
NaOH (100%)	0.1	10.62	0.01
Interest and tax on raw material	-	-	0.88
		<u>Material cost ..</u>	281.49
		<u>Manufacturing Expenses ..</u>	23.04
		<u>Total cost ..</u>	304.53
<u>Finished Dry Perbunan</u>			
Perbunan Latex	100	304.53	304.53
NaCl	153.7	1.60	2.55
Talcum	1.3	8.20	0.11
		<u>Material cost ..</u>	307.19
		<u>Expenses of mfg. ..</u>	19.15
		<u>Total cost ..</u>	326.34

Manufacture of Miscellaneous
Buna S - Type Polymers at Leverkusen

Dr. Holzrichter, who was in charge of production polymerization at Leverkusen, supplied the information contained in this report.

Types:

The following copolymers were manufactured at Leverkusen on a production basis:-

Buna SS - described in Hüls report

Buna SSE (E for Eisen) - same as Buna SS, except that iron-free water is used in the polymerization charge and oxyeresyl camphan is used as antioxidant. The product is used for pharmaceutical goods such as stoppers for medicine bottles. Leverkusen was the only plant which fabricated articles from Buna SSE.

Buna SSGF (GF for Geruch-und Geschmack-frei) - same as Buna SS but better degassing and better washing to remove odors. Product is used for milk, liquor and other types of bottle caps.

Buna SW (W for weich) - 90/10 butadiene/styrene copolymer with low Defo value. Said to be made for cable insulation requiring low temperature flexibility.

Production Procedure:

The manufacture of speciality Buna S-type synthetic rubbers is conducted in the same two buildings used for Perbunan production. Usually the polymerizations are batch-wise operations conducted in 20 cubic meter vessels with 30 cubic meter blown-down tanks in which antioxidant is added. Occasionally, however, Buna SSGF was prepared in the old small experimental continuous unit which had been used formerly to pilot-plant the large production continuous procedure. This small continuous unit consisted of five long cylindrical vessels agitated by wing shaped paddles which extended up along the walls of the vessels. The latex prepared batch-wise is accumulated in large holding tanks after degassing, and is then

transferred to the adjacent building where it is coagulated, washed, and dried continuously. The same type of glass tube for coagulation, fourdrinier for washing, and oven for drying is used as is used for Buna S and Perbunan.

Polymerization Formulae:

<u>Buna SSE</u>			<u>Parts by weight</u>
Butadiene	50
Styrene	50
Treated Water (Iron-free)	..		140
*Nekal BX	3.2 (calculated on basis of 100% solids)
Linoleic acid	2.0
NaOH	0.45
K ₂ S ₂ O ₈	0.25

The reaction is carried to 62% conversion in approximately 30 hours at 40-45°C, 3% oxyeresyl camphan is added as antioxidant, and coagulation is done after degassing. The oxyeresyl camphan is a non-staining antioxidant which permits heat softening of the polymer. It is not as good an age-resister as is phenyl-beta-naphthylamine. Coagulation is accomplished as follows, using iron-free water for coagulation and washing:

An 18% NaCl solution is added first at the rate of 40 to 60 kg of NaCl per 100 kg of dry polymer. Then a stream of 10% acetic acid is run in at the rate of 10 liters of glacial acetic per 100 kg of dry rubber.

Approximately 5 to 10 tons of Buna SSE have been produced per month with a Defo value of approximately 3500.

*Nekal BX containing 65% solids.

<u>Buna SSGF</u>			<u>Parts by weight</u>
Butadiene	50
Styrene	50
Condensate water	14.0
*Nekal BX	3.2 (calculated on basis of 100% solids)
Paraffin fatty acid	0.5
NaOH	0.2
K S O 2 2 8	0.25
**Diproxid	0.09

At reaction temperature of 40-45°C, the polymerization requires approximately 30 hours. When 62% conversion is reached, the latex is blown down to the receiver tank where 3% phenyl-beta-naphthylamine is added.

Extra care is exerted to remove all unreacted monomers. CaCl₂ is used for coagulation in a 3 to 5% solution at the rate of 5 kg of dry CaCl₂ per 100 kg of dry polymer. At times, however, NaCl and acetic acid have been used in the same proportions and amounts used for Buna SSE. A thimer band is formed on the fourdrinier machine so that the polymer can be washed more thoroughly.

Buna SSGF is produced in the quantities of 50 to 60 tons per month when the need requires it. The product has a Defo value of approximately 3000.

<u>Buna SW</u>			<u>Parts by weight</u>
Butadiene	90
Styrene	10
Condensate water	14.0
Nekal BX (Dry)	4.0

*Nekal BX containing 65% solids.

**Diproxid is diisopropyl xanthogen disulfide.

<u>BUNA SW (cont'd)</u>	<u>Parts by weight</u>
NaOH	0.2
K ₂ S ₂ O ₈	0.2
*Diproxid	0.33

Diproxid is added in three equal charges at the start, at 20% and 45% conversion.

The polymerization requires approximately 60 or 70 hours to reach 60% conversion. The latex is transferred to receiver tank where 3% phenyl-beta-naphthylamine is added. After monomer recovery, the latex is coagulated with a 5% solution of CaCl₂, using 10 kg of dry CaCl₂ per 100 kg of dry polymer.

Buna SW has a Defo value of 600-800 as it comes out of the drier.

Production Data in Tons

	<u>1939</u>	<u>1940</u>	<u>1941</u>	<u>1942</u>	<u>1943</u>	<u>1944 (to 26 Oct.)</u>
Buna SS	403	193	46	112	334	None
Buna SSE	-	-	39.2	32	118	80
Buna SSGF	-	-	79	29	337	288
Buna SW	-	-	-	-	193	242

In 1941, Buna SS production was started at Hül's, explaining the reduction in production at Leverkusen. Hül's production was hampered by bombing in 1943, so Leverkusen started producing again.

*Diproxid is diisopropyl xanthogen disulfide.

London, May 2nd, 1945.

This is a preliminary report on the investigation of Target No. 22/2 located at Leverkusen.

The investigation was made on April 24th, 25th and 26th, 1945.

The team leader was E.T. Handley and the team members were:

D.S. Garvey
R.D. Juve
N.R. Rowzee

Dr. Monrad and J.E. Troyan joined Mr. Fennebresque for an investigation of Target 22/82 located at Schkopau on April 24th so were not members of the team investigating Leverkusen.

Except for minor bomb damage, the Central Research Laboratory for Rubber was in good condition. The small tire factory (150 tires per day) was also in good condition. The Buna "N" plant was not so fortunate but was not badly wrecked.

Dr. Konrad Manager of the Central Research Laboratory was on hand and very co-operative. Also most of his staff was available and as Exhibit No. 1 we are attaching a list of these people.

The first day of our investigation we requested that certain information should be prepared for us and we are attaching copies. In addition, we went over their files and selected 2 - C.I.O.S. bags of files, mostly recent research reports. We were able to bring these as far as Paris and should have them in London this week. Our final report will include this information.

We are listing below the various reports we brought back with us:

- Exhibit No. 2. "Zeichenerklärung des Lageplanes"
3. "Zusammensetzung und Eigenschaften der im Mandel befindlichen Buna-Arten"
4. "Merkblatt - Buna S Type III"
5. "Buna SW"
6. "Buna SR"
7. "Richtlinien zur Prüfung von Polymerisaten"
8. "Tire Specs"
9. "Diene"
10. "Merkblatt für Desmodur R"
11. "Plastikator DO"
12. "Plastikator RA"
13. "Plastikator RA"
14. "Koresin"

- Exhibit No. 15. "Plastikator 88"
16. "Plastikator 89"
17. "Plastikator III"
18. "Renacit"
19. "Renacit I"
20. "Renacit II"
21. "Renacit II"
22. "Renacit III"
23. "Renacit als Regeneriermittel"
24. "Produkt LSII"
25. "Sonderdruck aus Gummi-Zeitung und
Kautschuk"
26. "Sonderdruck aus der Zeitschrift Kautschuk"
27. "Preise der wichtigsten Hilfsprodukte
für die Reifenherstellung"
28. "Polymerisation im Stromungsrühr"
29. "Fabrikation von Bunareifen"
30. "Desmodur-R"
31. "Desmodur-R"
32. "Desmodur-R"

E. T. HANDLEY

TYPES OF BUNA POLYMERS. LEVERKUSEN.

From information supplied by Dr. Holzrichter at Leverkusen, and from miscellaneous documents obtained at Huls, Schkopau and Ludwigshafen as well, it was ascertained that the following synthetic rubbers were prepared in Germany.

Buna S1 - Butadiene-styrene (70/30 charge ratio by weight) copolymer containing 2% linoleic acid; conversion about 60%. Originally prepared at Schkopau. Defo number about 4300.

Buna S2 - Same as Buna S1, but carried to about 55% conversion. Made at Huls the difference between S1 and S2 was relatively small, and was expected to disappear in time. S1 was a "bulkier, heavier" product than S2, and showed better fusion during vulcanization.

Buna S3 - Butadiene-styrene (68/32) copolymer, containing 0.5% paraffinic fatty acid, 0.1% Diproxid; conversion about 58%. Defo number approximately 3000. This polymer is softer than the original S1 and S2 type, and results in a large improvement in compounding operations. Better mixing, lower power requirements, and superior tack and adhesion are among its advantages. Vulcanized polymer shows essentially same physical properties as the Buna S1 and S2.

Buna SS - Butadiene-styrene (46/54) copolymer. Contains 3% linoleic acid; conversion 55%. Has better processability (smoother extrusion for tubes and cable) than the S Bunas; and higher tensiles in gum stocks. Elongation and cold resistance are inferior because of high styrene content. Defo number about 3700.

Buna SSGF Butadiene-styrene (50/50) copolymer, contains 0.09% Diproxid and no fatty acids; conversion 60%. Defo number is 3300. Product is washed thoroughly for taste-free and odor-free applications, especially in food industry.

Buna SSE - Butadiene-styrene (55/45) copolymer, containing 2.5% linoleic acid, 0.01% Diproxid; conversion 90%. Defo about 2400. Made free of iron by careful treatment of water. Stabilized with non-staining antioxidant, oxyeresyl comphan used for pharmaceutical applications and certain cements.

Buna Sw. - Butadiene-styrene (90/10) copolymer, containing 0.33% Diproxid; conversion 60%. Defo is 650, so polymer requires no heat treatment. Because of high butadiene content, has better cold resistance than usual Buna S. A report by Dr. Konrad at Leverkusen indicated that 0.5% paraffinic fatty acid was included in the recipe, which is in disagreement with the actual production formula by Dr. Holzrichter.

Buna SR Blend (50/50 by weight) of Buna S and Buna R. Latter type is Buna S carried to 96% conversion by reacting beyond 50% conversion at 80° C. Better processability (mixing, milling and tubing) than Buna S or S3. Has fair cold resistance, intermediate between SS and S. Made at Defo 3500.

Buna N. Butadiene-acrylonitrile (74/26) copolymer. Contains 0.2% paraffinic fatty acid, 0.33% Diproxid; conversion 75%. Defo number about 2350. Oil resistant rubber for usual applications.

Buna NN Butadiene-acrylonitrile (65/35) copolymer, using Mesapon N (in place of Nekal BK) and 0.39% Diproxid; conversion 70%. Defo number 3200.

Buna 85 Potassium - catalyzed mass polymer of butadiene. Defo 1400 used in making hard rubber with greater chemical resistance and higher heat stability.

Buna 32 Sodium - catalyzed mass polymer of butadiene (Mol. wt. about 10,000). Softener for Buna S which adds some tackiness, also used in varnished (Perivinane).

Buna M - Experimental butadiene - methacrylic acid ester copolymer. Good plastic deformation and age-resistance.

RUBBER TESTING AT LEVERKUSEN

The description of the building and organization of the rubber laboratory are given in another section of this report. This section deals only with rubber testing and polymer evaluation.

Equipment was available for running practically any type of rubber test which has had reasonably wide acceptance. Development work was conducted on new tests, both theoretical and empirical. Many types of product tests were made. It was possible to make almost any type of product from bottle stoppers to tires in the Research Laboratory. This was in addition to the pilot plant which was capable of producing about 300 tires per day. All equipment was the best that could be obtained and was set up with adequate space for convenient operation.

The extent of this work is well illustrated by the following outline of space and machinery.

Basement

- A - Store room
- B - Weighing room for rubber manufacturing research.
- C - Air raid shelter

Ground Floor - Rubber Manufacturing Research

- A - Mill Room.
 - Internal mixer
 - Refiner
 - Reclaiming Establishment
 - Preparation of hard rubber dust
 - Storage for stocks
- B - Calender room
- C - Tube machine room
- D - Presses for molded goods and conveyor belts
- E - Laboratory
- F - Production control
- G - Establishment for thermal break down
- H - Tire vulcanization

- J - Tire building. - tire development section
- K - Tire testing
- L - Spreading machines
Cord impregnation machine
Mixer for rubber solutions
- M - Finished good storage and shipment
- N - Electric switches and transformers

Mezzanine Floor - Rubber Production Research

- A - Preparation of technical hose and cable
- B - Built up articles, rubber shoes
- C - Stamps, boring, cutting of finished goods
- D - Fine machine workshop
- E - Constant temperature and humidity room (Klimaanlage)
- F - Research room for latex working
- G - Sample room

Technical Rubber Utilization

- I a - Room for dynamic measurements
- I b - Room for electrical measurements
- I c - High tension establishment
- I d - Test standard

First Floor

Testing and Customer Service Section

- A - Mill room for white and colored mixings, laboratory tube machines and calenders.
- B - Mill room for black mixings
- C - Preparation of mixings for vulcanization
- D - Curing presses,
Vessel for vulcanization in hot air and steam
Thermal breakdown
- E - Stamping room
- F - Testing room
- G - Aging establishment
- H - Laboratory spreading machines, internal mixers, and immersion apparatus

- J - Offices for visitors
- ~~K - Laboratories for optical investigations~~
Testing of auxiliary materials, pigments
and accelerators
- L - Laboratory of the testing division
- M - Registrar
- N - Writing room
- O - Laboratory for customer service
- P - Room for special work

Second Floor

Chemical Laboratory

- A - Laboratories
- B - Room for special work
- C - Room for physical-chemical measurements
- D - Glass blowing room
- ~~E - Technical research room~~
- F - Store room
- G - Library and sitting room
- H - Exhibition room
- J - Offices of leaders
- K - Secretariat
- L - Offices

Testing and Development Division

- M - Laboratories
- N - Textile laboratory
- O - Latex laboratory

Third Floor

- A - Resting and eating room
- B - Dressing room for men
- C - Bath for men
- D - Dressing room for women
- E - Rest room and bath for women
- F - Reserved - temporarily store room
- G - High pressure laboratory

Discussion of Tests

Most of the operations and tests were conducted by procedures which are well known and fairly well standardized. It is obviously undesirable to review these in detail here. They are described in detail in the various documents. A few have been selected for special comment.

Mills. There were several mills with the rolls independently driven by variable speed motors.

Durometers, were set to be read with an automatically applied, dead weight load. Some were set up for use above and below room temperature.

Stress-Strain and Rebound were both run on standard Schopper machines, some of which were set up to be run above and below room temperature.

Structure or Tear Test. The so-called structure test was really a tear test. Five standard cuts were made on the inside of opposite sides of a Schopper ring and the tensile determined on a Schopper machine in which the revolving drums were replaced by hooks. It was thought that a comparison of this value with the standard tensile value gave a measure of structure in the compound.

Strip Flex Test. In this test strips from a tensile sheet are repeatedly bent double and released.

Modified Torrance Flex Test. In this test strips cut from a tensile sheet were mounted on the periphery of a wheel. At each revolution they were bent by rubbing on a bar. It was modified by molding a grooved test specimen and by replacing the bar with a wheel.

Static Fatigue, was determined either at constant load or constant elongation. A dumb bell test specimen could be extended under a deadweight load for an indefinite period. Alternatively it

could be stretched to a definite elongation and held there. A third possibility was to extend by a definite load and then hold at the elongation attained.

Dynamic Fatigue - Rotating Rod. For this test the specimen is a cylinder about one inch in diameter and ten inches long. The clamp at one end can be driven to rotate this rod. The clamp at the other end can be swung around so that the rod is bent back to form an angle of about 75° . By a system of weights and pulleys this torque keeping the rod bent is maintained constant. Failure occurs at the apex of the angle. The test was used in three ways: (1) as a straight fatigue test, (2) with a knicked specimen for cut growth, and (3) with a specimen molded from two pieces so that the junction is in the middle as a test for fusion during cure.

Structure Stability - Static. In this test a cylinder is compressed under constant load and the compression curve obtained. Then the load is released and the recovery curve obtained. This test could be run both at high and at low temperatures. Comparison of such curves was used as one measure of the freezing point of the different rubbers.

Abrasion Test. While several of the standard abrasion tests were used, the favorite was one in which a small cylinder was pressed against emery paper on a rotating drum. Variable loads could be put on the specimen. During each revolution the specimen was lifted up and then dropped on the drum.

Dynamic Modulus and Hysteresis. Considerable emphasis was placed on hysteresis under constant load and on dynamic modulus. Such tests were run at different temperatures and showed considerable variation with temperature.

Electrical Tests, were also run at different temperatures and again there was considerable variation with temperature.

Plasticity. The Defo machine was preferred for plasticity measurement. It was necessary to run

six specimens on each stock, three as approximations and three for accurate values.

Schopper Detrition, was used extensively for measuring heat build up and stability for tire rubbers.

Product Tests. Many product tests were run, such as those for shear mountings, couplings, hose, tires, etc.

Polymer Evaluation

A definite procedure for the evaluation of polymers had been established. It required 2-3 kg. of polymer and they felt that this much was needed. The procedure is summarized here and the details are given in Document No.

Raw Material Properties. The polymer was examined for condition, color, smell, and volatile content. The Defo value was determined at 30°C. Solubility and viscosity were determined before and after milling. Storage stability, as measured by Defo and solubility was measured after 4, 8, and 12 weeks at room temperature and after 2 and 4 weeks at 50°C.

Ease of Breakdown was determined by milling and by thermal breakdown. The change in Defo on storage after breakdown was also measured.

Preparation and Properties of Mixtures. Three types of compound were used:- tread, carcass, and pure gum. Millability was determined on the tread stock using index numbers to indicate behaviour of the rubber alone, after softener addition, after black addition, and the condition of the sheet one hour after it was cut from the mill.

Batch Plasticity, was determined at 80°C.

Tubing Quality, was determined by running the tread stock through a small tube machine with a small

tread profile with head temperatures 50, 75 and 100°C. Appearance, length and weight per minute were observed.

Calendering was done on a small calender under carefully controlled conditions at different temperatures. Calender temperature, shrinkage after 5 and 24 hours, and surface appearance after 24 hours were reported.

Tack was measured by pressing calendered sheets together under constant load and checking the adhesion by a hard pull. An index of tack was used.

Solubility of the carcass compound was determined in iso octane.

Vulcanization and Physical Properties.

Cure. Test samples were cured 30, 60 and 90 min. at 110°C. for scorch. In addition the tread stock was run through a Marzetti plastometer at high temperatures. For quality cures were run at 20, 40, 60, 80 and 100 min. at 133°C.

Fusion was measured by the bent, revolving rod method.

Mechanical Properties. Tensile, modulus at 300%, and elongation were determined on Schopper machines. The Schopper tear (structure) test was also used. Rebound was measured at 20° and 70°. Hardness was determined on a Shore durometer with a dead weight.

Static Elastic-Plastic Properties, were determined by applying a load to a cylinder at different temperatures. The height of the cylinder was measured 1 second and 1 hour after the load was applied and 1 hour after it was released. Dynamic hysteresis and modulus were also determined.

Aging tests were run in the Geer oven at 100°C. for 1, 3 and 7 days. Bomb aging was used only in special cases.

Swelling tests were run in benzene, iso-octane, and water. The change in mechanical properties after swelling was also measured.

Electrical Properties, were measured as a special compound pigmented with talc and clay. Specific resistivity, dielectric properties, and breakdown voltage were measured after drying over P_2O_5 and after 24 hours in air saturated with water at $20^{\circ}C$.

Special Tests such as low temperature behaviour, ozone and weather resistance, gas permeability, heat conductivity and so forth were run in special cases only. For tire rubbers it was necessary to include Schopper detrition, flex life, and low temperature resistance.

Evaluations had to be made by experienced men on the basis of the above tests.

Polymerization Research at Leverkusen.

An unsigned Leverkusen document dated 27 August, 1942 presented the following description of the evolution of Buna series of synthetic rubber.

By 1926 - 1927 a great deal of research had been done in Germany concerning the polymerization of butadiene and isoprene in which the hydrocarbon was either mass polymerized or polymerized in latex emulsion. The latter method of polymerization was discovered by Hofman (D.R.P. 234672, 235129) and used albumin, blood serum, starch, milk, etc. as emulsifying agents. The mass polymerization method was discarded, however, since the yields were low and the product unsatisfactory. From the beginning in 1927, important progress was made in the emulsion method by using saline emulsifying agents such as soap and Nekels. In the I.G. Werke Ludwigshafen it was thought that a definite pH was important, while at Leverkusen it was thought that a definite weight of oxygen or oxygen-producing material (D.R.P. 511145, 15 Jan. 1927) should be used. The latter remains today as the working method. The new polymerization method was developed in Leverkusen by Lecher, Konrad, Bachle, Schwerdtel, Meisenburg, Dennstedt, and others. With it a procedure was created to polymerize the hydrocarbon to higher yields in shorter time without the use of heat. The quality of the butadiene and isoprene polymers was deficient, and continued work in this direction always led to negative results.

A decided turning-point in the development of synthetic rubber occurred when study was directed towards vulcanization. The effort to duplicate the natural rubber structure in polymerization had been unsuccessful. It was found, however, that considerably more improvement of polymerization quality resulted with synthetic rubber when pigments were added and the compound was cured than was the case with natural rubber.

Work was first started with 2,3 dimethyl butadiene synthetic rubber, but satisfactory tensile values had never been obtained despite the efforts of a year-long research in vulcanization. By the incorporation of pigments to the rubber the tensile and elongation values were raised by 100% and sometimes higher. This result must be viewed as fully new since with natural rubber the quality improvement is very small and in general with carbon blacks an increase of the tensile follows only at the expense of elongation. The isoprene and butadiene

emulsion polymers as well as the isoprene sodium polymer was vulcanized in this way, and a partial improvement in quality was obtained. These results were organized and announced by the patent D.R.P. 578965, 11 June, 1927. Broader protection was taken on the use of other pigments, as for example, zinc oxide, magnesia, etc. which were partially efficient although inferior to gasblack. The discovery of the quality improvement with carbon black was of considerable practical importance. Numerous black vulcanizates were prepared in December, 1927 with an isoprene-dimethyl butadiene emulsion polymer of inferior quality, which had been polymerized with oxygen producing agents, by vulcanization in a mixture with gas black and were compared to a gas black-free vulcanizate. The product with black had a 600-800% improvement in tensile and elongation. It resulted in not only an unusual increase in tensile but also a noticeable improvement in the elongation, which had not been observed previously either with natural rubber or with the synthetic rubber. A thorough investigation showed that this was dependent on the copolymer structure and, for example, can be attained with butadiene-dimethyl butadiene in equal amounts and curing the copolymer into a vulcanizate with gas black. This was basic new knowledge, since it was established thereby that in a copolymer no mixture of polymers of the individual components must exist, but a new chemical individual. This was announced in the patent I 33275 IV/39 of 20 Jan. 1928 where the preparation method of this copolymer was described in combination with the black vulcanization for the purpose of making of high quality rubber products, especially tires. Later this announcement had been withdrawn since the general earlier announced black vulcanization method (D.R.P. 578965) could not be clearly enough defined in regard to the part of the method dealing with polymerization in the earlier patent of I.G. Farbenindustrie. In this earlier synthetic rubber research Hofman had not sufficiently described the method or of the amounts of the three hydrocarbons (D.R.P. 255679 of 1 April 1910). Any advantage in quality in contrast to the separately polymerized rubbers was not established so long as the new vulcanization method was not put to application. Also, satisfactory polymers could be obtained only if a definite ratio of the elastic component (butadiene or isoprene) to the inelastic component (dimethyl butadiene) were used so that an elastic

copolymer resulted. This knowledge had not been presented in patents at any time previously. Today no doubt can exist that this research had introduced the beginning of the new epoch of synthetic rubber.

The sodium polymer of butadiene prepared 18 years ago by Harries was not developed much further, the work on which had been done by Klein of Leverkusen and other workers of Ludwigshafen and further developed by Zieser and Stocklin of Leverkusen as well as by Schmidt and co-workers of Ludwigshafen by black vulcanization. The best products of these polymerizations, from which the current Buna 85 and 115 were prepared finally reached noteworthy quality and led later to the emulsion polymerization. In I.G.Werke Ludwigshafen an oleic acid-containing butadiene emulsion polymer was prepared by Heuk which found interest in a short time although it soon became replaced by a genuine copolymer.

The similarity of the "black effect" of sodium butadiene rubber with that of the copolymers made it plausible that both types had a similar structure. In 1911 Harries had established that the sodium butadiene rubber could not be polymerized "normal". He had to conclude from the study of the ozone breakdown that it contained a small amount of non-rubber constituent. The superiority which the leather-like inelastic dimethyl butadiene polymer produced in rubber mixtures brought about the thought that after such copolymers had been prepared they contained not only rubber hydrocarbon but also polymers which were not rubber-like. This can be seen for example by the polymers of simple vinyl compounds which, polymerized by itself, yields artificial materials of resinous nature. This led to the first research on copolymerization of isoprene or butadiene with styrene and led soon to the fixation of the proper ratio of the two ingredients. The products of isoprene or butadiene polymerized with styrene were superior to the previously prepared synthetic rubber when vulcanized and produced a synthetic rubber which was no longer inferior to natural rubber. The present Buna S was prepared and is protected by the patent D.R.P. 570980 and 532456 of 21 July 1929.

By this important research the general use of a simple vinyl compound for the preparation of high quality rubber was disclosed for the first time. The further perfection indicated that only vinyl compounds with an unsaturated group of an active double bond in the neighboring position were satisfactory for

copolymerization with butadiene. To this work Konrad, Tschunkur, Meisenburg, Kleiner and others at Leverkusen devoted themselves.

By the polymerization with the vinyl component the properties of the products can be varied so that the likelihood exists of producing a number of special types of buna, as for example the gasoline- and oil-resistant Buna N by the use of acrylonitrile (B.R.P. 658172 of 26 April 1930).

The development of a good synthetic rubber came about when the original striving for a duplication of natural rubber was discarded and an effort was made to create a synthetic rubber of special structure to have unique properties when cured in a compound. Work which was taken up in the laboratory at I.G. Werke, Leverkusen has already furnished some information on the nature of the synthesis, but much remains to be done along this line. Particularly, the reason should be found for the great improvement in the properties of copolymers by pigmentation. Also, the processing properties of Buna on the mill and in extrusion allow for much improvement. It was Koch at Leverkusen, working with the rubber factories, who developed the thermal breakdown procedure whereby the product was rendered more plastic. Much improvement in this direction can still be made, however.

In conversation with Dr Stöcklin at Leverkusen, it was found that no antioxidant superior to phenyl beta naphthylamine as an aid in heat softening and as an age-resistor had been discovered. Oxy-cresyl camphan is satisfactory for non-staining Buna, but is somewhat inferior to phenyl beta naphthylamine as an age-resistor. It is the best non-staining antioxidant which has been found.

The following materials have been studied at
Leverkusen for synthetic rubber :

DIENE.

(Polymerized alone or copolymerized with active
vinyl compounds).

Butadien 1,3
1 Methylbutadien 1,3
2 Methylbutadien 1,3
2,3 Dimethylbutadien
1,3 Dimethylbutadien
1,1 Dimethylbutadien
1,4 Dimethylbutadien
1,1,4,4 Tetramethylbutadien

4 Cyanbutadien 1,3
1 Phenylbutadien 1,3

2 Athoxybutadien
1 Athoxybutadien
1 Acetoxybutadien
2 Acetoxybutadien
2 Phenoxybutadien

1 Chlorbutadien
2 Chlorbutadien
2 Chlor, 3 Methylbutadien
1,2 Dichlorbutadien
2,3 Dichlorbutadien
1 Phenyl, 2 Chlorbutadien

VINYL COMPOUNDS.

(Copolymerized with dienes, especially with 1,3 buta-
diene, 2,3 dimethylbutadiene, and 2 chlorobutadiene.)

Propylen
Isobutylen
Amylen

Styrol
Vinylnaphtalin
Stilben
a-Methylstyrol
p-Phenylstyrol
p-Methylstyrol
p-Athylstyrol
p-Chlorstyrol
Dichlorstyrol
omega-Methylstyrol
Nitrostyrol

Vinyl Compounds - Continued.

Vinylpyridin
Vinylfuran
Vinylcarbazol

Vinylchlorid
Vinylbromid
2 Chlorpropylen
Allylchlorid
Vinylidenchlorid
1,1 Dichloräthen
Trichloräthylen

Cyclopentadien
Inden

~~Vinylacetat~~
Vinylisobutyläther
Vinyläthyläther

Acrolein
α-Methylacrolein
α-Athylacrolein
α-Isopropylacrolein
α-Hexylacrolein
α-Phenylacrolein
Crotonaldehyde

Vinylmethylketon
Vinylisopropylketon
Vinylphenylketon

Benzalacetone
p-Methylbenzalacetone
p-Athylbenzalacetone
p-Nitrobenzalacetone

Acrylsäure
Zimtsäure

Acrylsäuremethylester
Acrylsäureäthylester
Acrylsäurepropylester
Acrylsäureisobutylester
Acrylsäuredodecylester
Acrylsäuredekalolester

Products studied on Pilot-Plant Scale - Continued....

2,3 Dimethylbutadien
Isopren
2,3 Chlorbutadien

POLYMERIZATION MODIFIERS.

Di-isopropyl-xanthogendisulfid
Di-isobutyl-xanthogendisulfid
Diisoceryl-xanthogendisulfid

Tolyldi sulfid

Hexylmerkaptan
Dodecylmerkaptan
Nonylmerkaptan

Athyl-thio-buten
Phenyl-thio-buten
Phenyl-thio-chlorbuten

Phenylchlorbuten
Nitrophenylchlorbuten

Tetrachlorkohlenstoff
Chloroform
Hexachloräthan

Phenyldiacetat
Tolyldiacetat

Triisobutylphenol
Dodecylphenol

Leinolsäure)
Ricinolsäure) und deren Ester
Holzölsäure)

omega-Methylstyrol
omega-Nitrostyrol

Inden
Fluoren

Methacrylsäuremethylester
Methacrylsäureäthylester
Methacrylsäureisobutylester
α-Isobutylacrylsäuremethylester
α-Phenylacrylsäuremethylester
α-Chloracrylsäuremethylester
α-Chloracrylsäureäthylester

Acrylsäurechloräthylester
Acrylsäurecyanäthylester
Acrylsäurecyanmethylester

Crotonsäureäthylester
Zimtsäureäthylester

Fumarsäurediäthylester
Fumarsäuredimethylester
Fumarsäuredichloräthylester
Muconsäurediäthylester

Acrylsäureamid
Acrylsäuremethylamid
Acrylsäurediisobutylamid
Acrylsäuremethylphenylamid

Methacrylsäureamid
Methacrylsäurediisobutylamid

Acrylsäurenitril
Methacrylsäurenitril

Cyansorbinsäuremethylester
Cyansorbinsäureäthylester
Cyansorbinsäurebutylester

PRODUCTS STUDIED ON PILOT-PLANT SCALE.

Butadiene copolymers with:

Vinylmethylketon
Isopropenylmethylketon
Acrylsäuremethylester
Acrylsäureäthylester
Methacrylsäuremethylester
Fumarsäurediäthylester
Cyansorbinsäuremethylester
Acrylsäurediisobutylamid
α - Methylacrolein
α - Äthylacrolein
Vinylnaphthalin
Vinylpyridin
p-Phenylstyrol

In addition to the general foregoing information, more detailed information is available in the Leverkusen research documents, particularly in the following:

"Elastizität und Chemische Konstitution Kautschukelastischer Stoffe" by Dr.P.Stocklin of Leverkusen, 15 July, 1943.

"Polymerisation und Polymerisatonaufbau von Dienen" - unsigned Leverkusen document.

"Stand der Anwendungstechnik auf dem Buna-Gebiet" by Dr.E.Konrad of Leverkusen, 1 March, 1944.

"Stand des Verfahrens der Polymerisation von Buna in Schkopau" by Dr.Wilhelm Klein, 25 July, 1944.