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Second Petrochemical Symposium on the
Development of the Petrochemical Industries in
Developing Countries

PET. SYMP. E/2

USSR, 23 - 31 October 1969

A SELECTION OF PROCESSES FOR THE MANUFACTURE OF POLYMER

PRODUCTS, PARTICULARLY OF SYNTHETIC RUBBERS^{1/}

by

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presented by

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SUMMARY

A SELECTION OF PROCESSES FOR THE MANUFACTURE OF
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A description is given of eight processes for the manufacture of polymer products, particularly of synthetic rubbers, most of these processes representing the latest status of development in the fields concerned.

1.0 Synthetic Rubbers

1.1 Styrene-Butadiene Rubber (SBR)

With a share of approximately 80 per cent, SBR has been holding a decidedly dominating position in the field of synthetic rubbers. Depending on the polymerization temperature, a distinction is made between hot and cold rubber. Cold rubber is the more recent type and exhibits improved

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characteristics. The Hüls process is conducted in aqueous emulsion at temperatures of about 5°C. A number of auxiliary chemicals are required and it is important to charge them in accurately measured amounts. Polymerization is performed in a cascade of agitated reactors. The charged monomers are reacted to only approx. 60 per cent conversion for reasons of product quality, thus involving monomer recovery on quite a large scale. The latex is coagulated and the product so obtained is washed, dewatered and dried.

The economics of a 26, 00 MT/yr. plant are reported in the discussion paper.

1.2 cis-Polybutadiene

Polybutadiene is an elastomer which, because of its outstanding abrasion resistance and good loading capacity for extender oil and fillers, has in the past few years achieved great importance as a raw material, especially in tyre manufacture.

By the Hüls-Bayer process 1,3-butadiene is polymerized at 20° - 50°C in benzene as a solvent in the presence of an organic aluminum/cobalt catalyst system and a modifier. If the product desired is a high-molecular-weight polybutadiene, which affords great advantages in oil and filler loading, use can be made of the molecular-weight jump reaction by the addition of a special catalyst. In this reaction, two or more of the polymer chains already produced are linked together. For finishing, the polymer solution is blended with water and the solvent is removed by steam stripping with resultant coagulation of the rubber. The coagulated product is dewatered and dried.

The cis-content of the polybutadiene is 96 - 98 per cent. The Mooney viscosity ML₄ is 47.

The economics of a 30,000 MT/yr. plant are reported in the discussion paper.

1.3 Polyisoprene

Polyisoprene is the synthetic reproduction of natural rubber. It exhibits almost the same static and dynamic test values. Polyisoprene lends itself particularly well to the manufacture of large tyres as well as of non-filled rubber products. As soon as isoprene monomer is available in major amounts and at reasonable cost, this type of rubber will gain considerably in importance.

High demands are placed on the purity of both the solvent and, particularly, the isoprene used in the polymerization.

By the Hüls-Bayer process polymerization is accomplished continuously in a series of stirred vessels in the presence of organometallic mixed catalysts in an aliphatic hydrocarbon as the solvent. After addition of stopper and stabilizer the catalyst compounds are washed out and subsequently the unconverted monomer and the solvent are removed by steam injection. The polymer crumb obtained is dewatered and dried.

97,5 per cent of the polyisoprene formed exhibit a 1,4-cis structure.

The economics of a 20,000 MT/yr. plant are reported in the paper.

1.4 Ethylene-Propylene Rubber (EPR and EPDM)

These modern rubber types, which are produced by co-polymerisation using Ziegler-Natta catalysts, are notable for outstanding resistance to aging, good performance characteristics, and high oil and filler absorption.

The anhydrous monomers ethylene and propylene and, where necessary, the ter component, i.e. the "diene", are co-polymerised in an inert anhydrous solvent in the absence of air. By the Hüls-Hoechst process this operation is continuous.

The unconverted monomers are recovered and recharged to the process. On addition of stopper and stabilizer the catalyst-compounds are washed out. On removal of the water the polymer solution is coagulated by steam injection and the solvent stripped. The rubber crumb obtained is dewatered and dried.

The economics of a 20,000 MT/yr. plant are reported in the discussion paper.

2.0 Other Polymer Products

2.1 Polybutene-1

Polybutene-1 has some important advantages over other polyolefines (polyethylene, polypropylene), viz., it is extremely resistant to stress cracking and exhibits low plastic deformation under long-sustained loads with the result that it has excellent creep rupture strength, even at elevated temperatures. An important field of application, therefore, is the pipe sector, where polybutene-1 can also be used to advantage in the manufacture of large-diameter pipe designed for elevated pressure and temperature service. Even at very high molecular weights polybutene-1 can satisfactorily be processed thermoplastically and permits the use of conventional processing methods such as extrusion and injection molding.

The polybutene process developed by Huls operates continuously in the presence of Ziegler catalysts. The feed material is a cracked gas containing approx. 50 per cent or more of n-butene-1 besides other C₄-hydrocarbons. Water, oxygen, sulfur compounds, acetylenes, and dienes must be excluded from the process. The C₄-mixture, having passed through polymerization, can be recycled.

The bulk of the polymer has the desired isotactic structure. The small proportion of atactic material can be withdrawn from the bottom of the distillation unit.

The economics of a 12,000 MT/yr. plant are reported in the paper.

2.2 Cyclododecatriene

Cyclododecatriene-1,5,9 is a readily available trimer of butadiene and has, for some years, been used as the basic material for the C_{12} chemistry, which commands increasing importance. So cyclododecatriene, by a route involving several steps, leads to lauryl lactam and polylauryl lactam (Hylon 12) or by severer oxydation, decane dicarboxylic acid can be produced, which serves as the starting material for the production of other polyamides and polyesters. Hexabromocyclododecane is added to the plastics to act as a flame retardant.

The Hüls process is conducted at 70°C and atmospheric pressure in benzene in the presence of Ziegler catalysts after the stabiliser has previously been removed from the butadiene. For deactivation of the catalyst, the crude product is treated with caustic soda solution. Then the benzene is distilled off and the cyclododecatriene purified by distillation.

The conversion is 98 per cent and the yield 89 per cent, based on the butadiene fed to the process.

The economics of a 12,000 MT/yr. plant are reported in the paper.

2.3 Polylauryl lactam

Compared to the known polyamide types, polylauryl lactam exhibits the lowest water absorption and has the best dimensional stability. Also, it possesses the lowest density, which amounts to savings in material.

On the other hand, it has an extremely high wear resistance.

The process developed by Hüls for the manufacture of polylauryl lactam proceeds from cyclododecatriene-1,5,9, which is hydrogenated to cyclododecene. This is oxidized with air to a mixture of cyclododecanol and cyclododecanone, which is then dehydrogenated to pure cyclododecanone. The cyclododecanone is converted with hydroxylamine to oxime, which is then rearranged to lactam using concentrated sulfuric acid.

Polymerisation of lauryl lactam is accomplished batchwise at 20 atm with the addition of an initiator. On polymerisation the reactor is emptied via spinnerets. The strands are cooled in a cooling trough and are pelletised. The pellets are screened, further dried and packaged. By thermal treatment the pellets can be post-condensated to give material of higher molecular weights.

The economics of a 2400 MT/yr. plant are reported in the paper.

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

The object of this paper is to present a number of the more recent material being produced selected from the large field of polymer products, which have a significant impact on modern living. Characteristically, most of these products employ the basic raw materials of petrochemistry as the starting point, the emphasis being clearly on C₄-hydrocarbons.

Our selection of subjects comprises:

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1.0 Synthetic Rubbers

The first four subjects refer to the field of synthetic rubbers and it seems appropriate to say a few words on these:

For more than fifty years research efforts throughout the world have been directed toward the development of economic synthetic rubber processes. As a major outcome of this work styrene-butadiene rubber (SBR), starting from Germany, acquired a dominating position which it still holds today.

In the late fifties it was found that with the aid of Ziegler-Natta type catalysts it is possible to build up novel rubbers, referred to as stereo rubbers, which exhibit regularity in spatial arrangement of the atoms in the macromolecule. These modern rubber types include polybutadiene, polyisoprene and ethylene-propylene rubber.

1.1 Styrene-Butadiene Rubber (SBR)

1.1.1 Process description (see diagram 1.11)

The cold rubber process in use on a commercial scale at Buna Werke Huls GmbH since 1950 is accomplished in aqueous emulsion at temperatures of around 5° C and at a pressure that keeps the butadiene in the liquid phase. Polymerisation is carried out in a cascade comprising several agitated reactors arranged in series, the heat of reaction being carried off by evaporation of ammonia in vertical tube evaporators incorporated

in a stirred tank polymerization reactor, and the latex is pumped
to a separator.

The separator is a vertical cylindrical vessel in which quality polymerization of styrene and butadiene
takes place. The separator is designed for 90% conversion of the hydrocarbons. For
the remainder of the converted hydrocarbons, the separator-staining latex is
fed to a vacuum stripper and then to a vacuum stripper to remove butadiene.

The butadiene-free latex is then stripped of styrene in a sieve-plate
column and the styrene-free latex is again sent to intermediate storage
with the addition of a stabilizer.

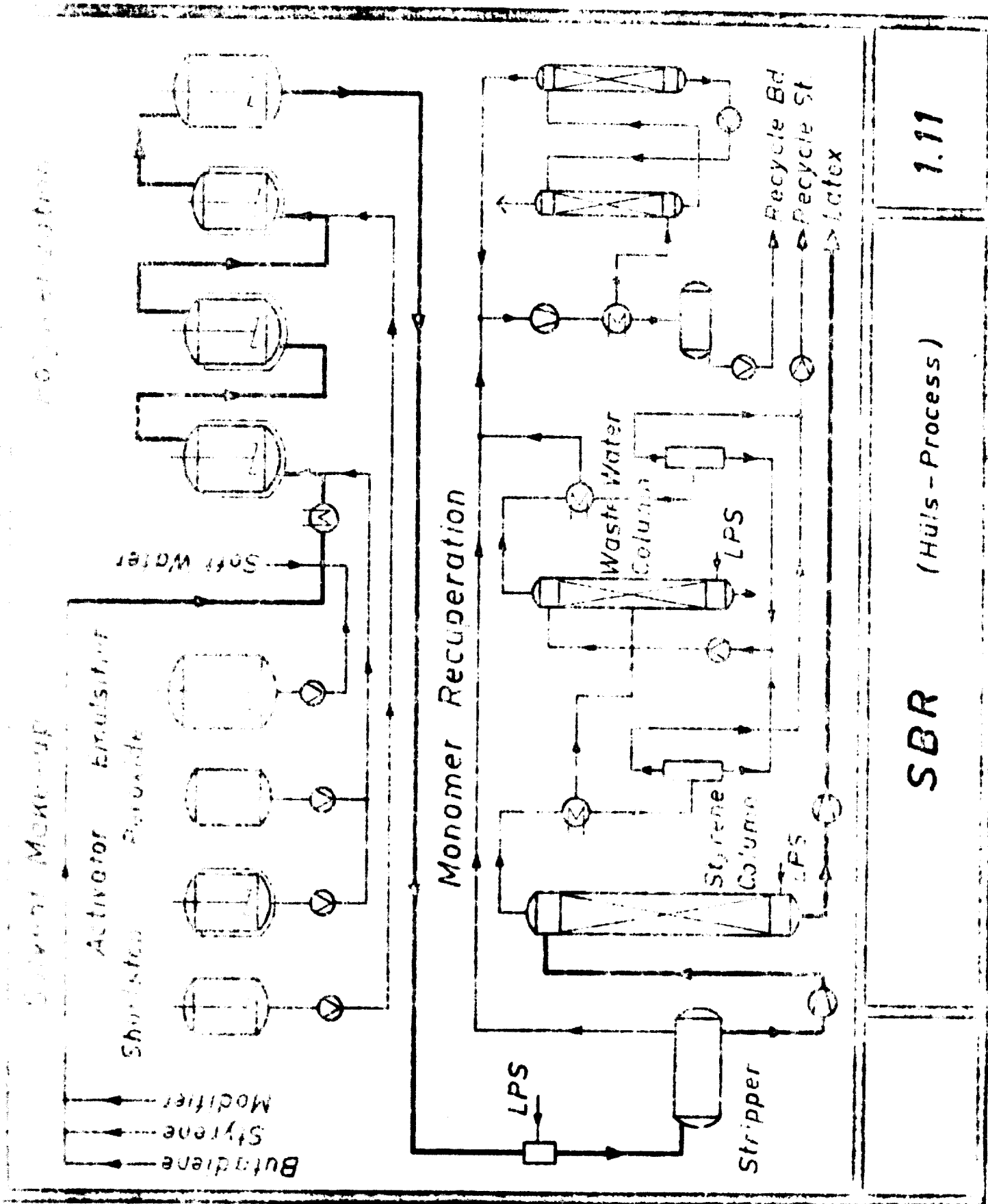
The two monomers recovered, i.e. butadiene and styrene, are worked up
in an appropriate manner and restored to a condition which permits their
reuse in polymerization.

For the recovery of solid rubber from the latex, the latter is
coagulated, washed, washed, washed and then largely deoiled, shredded,
dried, granulated, weighed and packaged. In the case of oil-exten-
ded latex, the oil is added to the SER latex before coagulation.

1.14 Concentration of Monomers

Gas chromatography analysis per 1 000 kg of rubber

Butadiene	928	kg
Styrene	242	kg
Monomers	1170	kg



SBR (Huls-Process)

1.11

Energy Required per 1 000 kg of rubber

Electric power (low tension)	252	kWh
Water (cold)	12	m ³
Steam (20° C)	40	m ³
Steam (4 atm)	3.5	metric tons (MT)
Compressed air (5 atm)	205	Nm ³
Nitrogen	13	Nm ³
Refrigeration (-5° C)	350,000	kcal

Energy Required per 1 000 kg of rubber

Man hours

Battery limits cost of a plant with a capacity of 10,000 MT/yr.

Approx. 2.9 million (in the Federal Republic of Germany). This figure does not cover monomer storage, finished product storage, engineering, financing, and other charges and lines to battery limits.

REFERENCES

1. Jersch: Kautschuk u. Gummi, Kunststoffe 21 (1968) (6) 299

2. Krüchel: Kautschuk u. Gummi, Kunststoffe 21 (1968) (9) 455

1.2.2.2. Polybutadiene (R BUNA CB +)

Polybutadiene is an elastomer which has recently gained particular significance in tyre manufacture as a result of its outstanding abrasion resistance and good swelling capacity for oil and fillers.

cis-Polybutadiene is prepared in solution with Ziegler type catalysts. In a 20,000 m³/yr. plant belonging to Stereokautschuk-Werke GmbH at Witten use is made of a cobalt catalyst in the manufacture of cis-polybutadiene.

The raw materials are as follows:

1,3-butadiene, organic aluminium catalyst, cobalt catalyst, modifier, benzene, short-stop, anti-oxidant. For high-molecular, oil-extended polybutadiene, a pump reagent and an extender oil will be required in addition.

1.21 Process Description (see diagram 1.21)

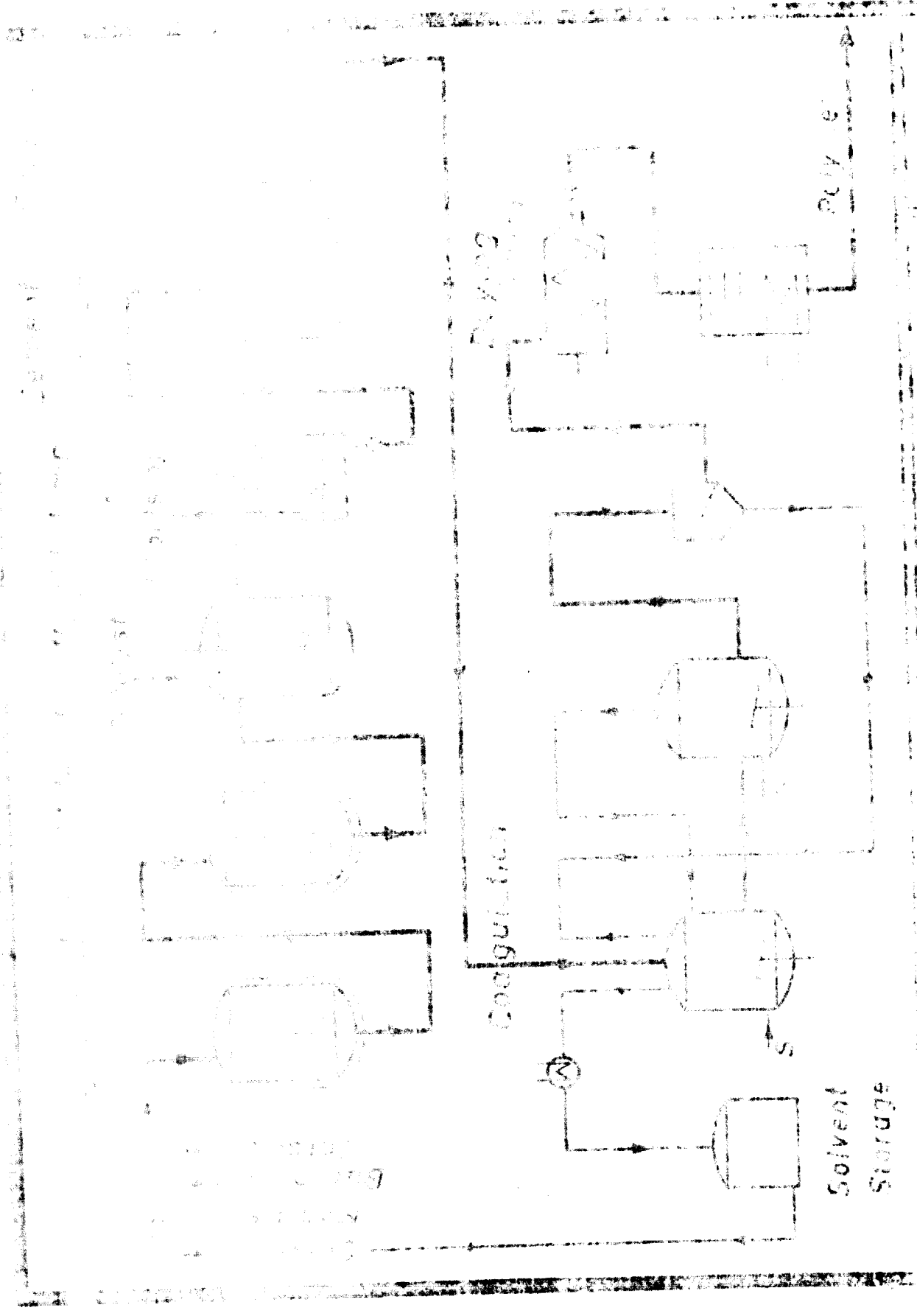
The feed materials are introduced into the first of a number of cooled vessels arranged in series. On leaving the last vessel, the solution polymerized to a conversion of 30 - 90 % is short-stopped and anti-oxidant is added to it. Polymerization is carried out at 20 - 50° C.

Before the solution is transferred to the finishing area, the catalyst constituents are passed into solution by the addition of water in an internal mixer. Rubber solution and wash water are then introduced into the coagulation system, where the solvent is stripped by steam. The rubber crumb is separated from water on a vibrating screen and is then further dewatered in a screw press. Residual water is removed in an air-circulation belt-type dryer. The dried rubber is then baled, each bale weighing 30 kg.

The cis-content of the polybutadiene amounts to 96 - 98 %. The Mooney viscosity is $MV_4 = 47$.

The solvent recovered from the coagulation system after water removal is recycled to the process after appropriate treatment.

*) BUNA CB⁺ is a product of Stereokautschuk-Werke GmbH u. Co. KG.



cis-Polybutadiene (Huls-Bayer-Process) **1.21**

For the manufacture of high-molecular, oil-extended cis-polybutadiene, a molecular weight-jump reaction, linking two or more polymer chains, is carried out after polymerization (and before chain-stopping and addition of anti-oxidant) by varying the catalyst system. Then, before finishing, extender oil is added. In the case of high-molecular polybutadiene more oil and anti-oxidant can be added than with normal polybutadiene, without adversely affecting the properties of the final product. This also improves other characteristics such as processibility.

1.22 Consumption Figures

Raw Materials Required per 1 000 kg of rubber

Butadiene	1010	kg
Benzene	45	kg
Chemicals	69.-	DM

Utilities Required per 1 000 kg of rubber

Electric power (low voltage)	400	kWh
Steam (4 atm)	5	MT
Compressed air (5 atm)	240	MT
Nitrogen (5 atm)	16	Nm ³
River water (20° C)	23	m ³
Refrigeration (-5°C)	330,000	kcal

Labor Required per 1 000 kg of rubber

3,4 man-hours

Battery-limit-costs of a plant with a capacity of 30,000 MT/yr. (2 lines of reactors, with provision for oil-extension) approx. \$ 6,25 million (in the Federal Republic of Germany). This figure does not include monomer storage, finished product storage, engineering, financing, land development and lines to battery limits.

1.23 Literature

E.F. Engel: Kautschuk u. Gummi, Kunststoffe
21 (1968) (4) 171

synthetic polyisoprene has achieved increasing attention as a replacement rubber. Polyisoprene is the synthetic rubber which most closely combines almost all of the static and dynamic properties of natural rubber. Its advantage over natural rubber is its greater processing latitude and, above all, the possibility of eliminating the degradation process by adjustment of the viscosity wanted by the manufacturer.

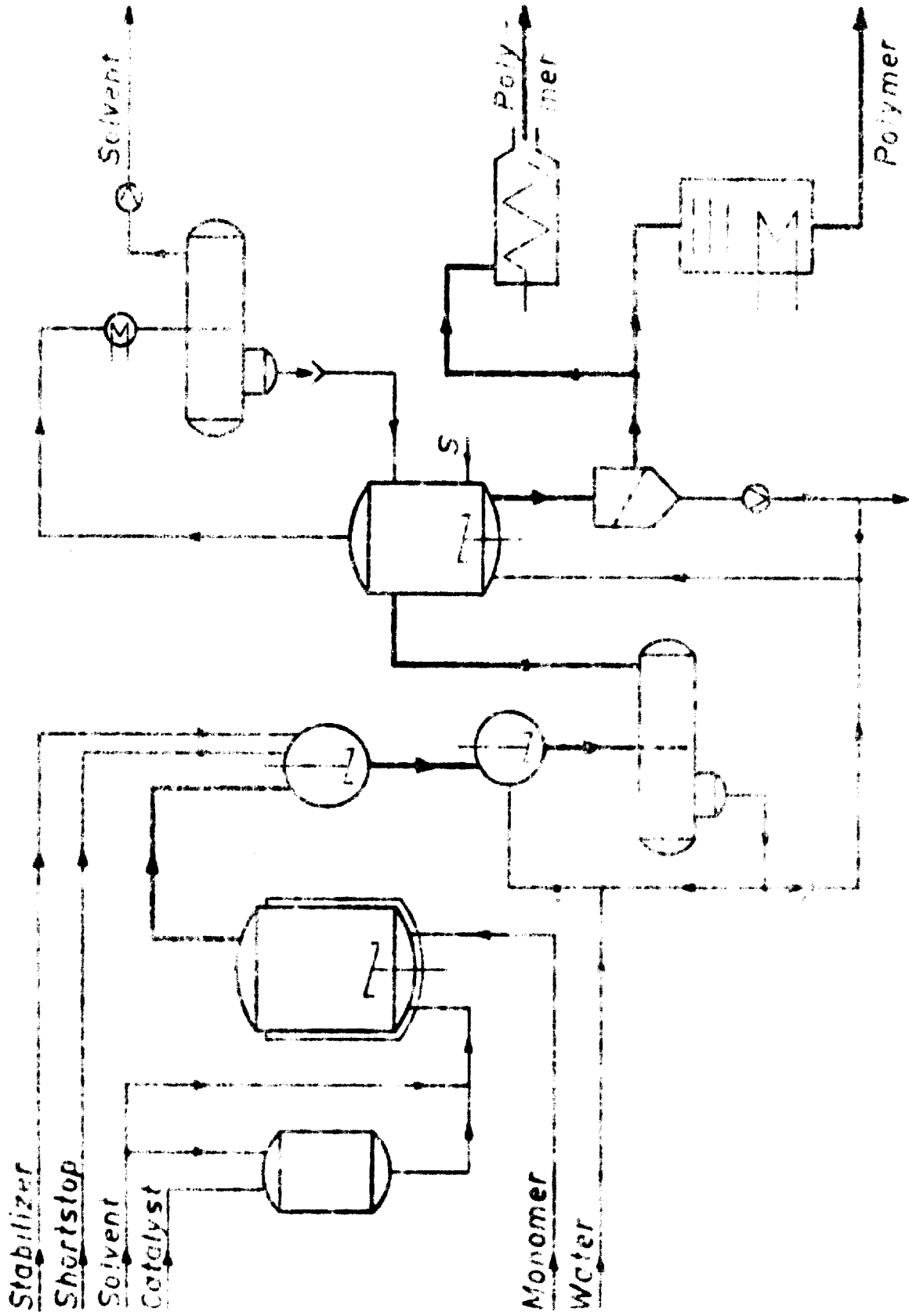
It is especially suited itself particularly to those applications which until recently were natural rubber's own domain, for example, the manufacture of tires, particularly of large ones. Polyisoprene can also be used in the production of technical rubber products, particularly in the form of films, as latex in dip-molding and impregnation.

The process for the manufacture of polyisoprene with an approx. 97% cis configuration is based on the use of organometallic mixed catalyst systems consisting of a combination of titanium tetrachloride and aluminum alkyls.

It is essential to use preferably of aliphatic hydrocarbons as the solvents. Aromatic hydrocarbons, ethers and compounds containing active hydrogen, as well as unsaturated compounds, acetylenes and organic sulfur compounds are excluded throughout the polymerization system. High yields are obtained on the purity of the solvent and particularly of the catalyst.

1.31 Process description (see diagram 1.31)

The feed materials isoprene and solvent along with the separately prepared catalyst system in the desired ratio are continuously fed into a first polymerization reactor of a line of reactors.



1.31

Polyisoprene (Huls-Bayer-Process)

The heat of the polymerization is carried off by means of a cooling liquid in a system of cooling jackets.

When the polymerization solution has left the reactor line, a short-stop and a stabilizer are stirred into the solution. After the washing operation and after separation of the wash water the polymer solution is passed to the stripper system, where the solvent and the unconverted monomer are stripped by steam and the polymer is dispersed as crumb in water. The vapors are condensed and passed to the separation vessel. On being dried and purified by distillation, the solvent-monomer mixture recovered is recycled to polymerization.

The aqueous crumb dispersion is passed over screens, where the crumb is separated from the water; this water is returned to the stripper system. Drying of the moist polyisoprene crumb is accomplished either in an apron-dryer or in a suitable screw press. The dried polyisoprene is pressed into commercial bales.

1.32 Consumption Figures

Raw Materials Required per 1 000 kg of rubber

Isoprene	1030	kg
Aliphatic solvent	80	kg
Chemicals	70.- to 100.-	DM

Utilities Consumption per 1000 kg of rubber

Electric power (low tension)	550	kWh
Steam (20 atm)	1	MT
Steam (4 atm)	8	MT
Compressed air (5 atm)	360	Nm ³
Nitrogen	24	Nm ³
River water (20° C)	300*	m ³
Refrigeration (-5° C)	330,000	kcal

Labor Required per 1 000 kg of rubber

5,1 man-hours

Estimate limits-costs of a plant with a capacity of 20,000 MT/yr (2 lines of reactors)

approx. \$ 6, 2 million (in the Federal Republic of Germany). This figure does not include monomer cost, finished product storage, engineering, financing, land development and final factory limits.

1.4 Ethylene-Propylene Rubber

The copolymerization of ethylene and propylene using Ziegler catalysts, on account of the statistical character of the polymer chain, gives rise to elastomers which have gained appreciable technical significance in the past few years. A distinction is made between

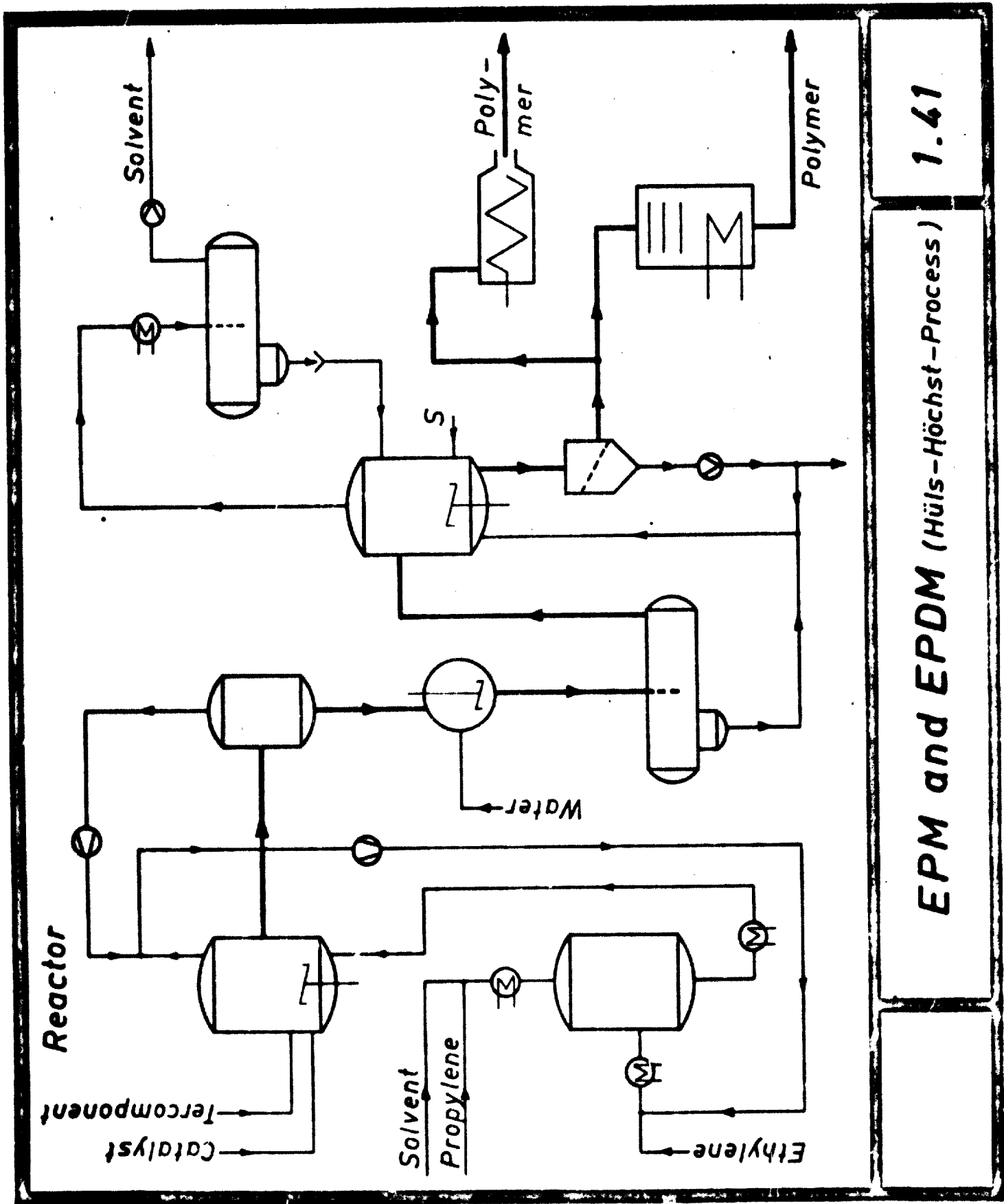
1. saturated ethylene-propylene rubber (EPN) and
2. unsaturated ethylene-propylene rubber (EPDM)

Whereas saturated EPN can be cross-linked by means of peroxides only, EPDM can - besides by means of quinones and peroxides - also be crosslinked with the aid of conventional sulfur and cobalt-donor-based systems as a result of the double bonds available (1 to 15 double bonds per 1000 C atoms).

Both EPN and EPDM exhibit excellent aging resistance and good performance characteristics. These features and high oil and filler absorption-capacity ensure wide applicability of EPN and EPDM in the field of technical rubber products. EPDM has already come into its own for use in sidewall compounds for automobile tyres. Tyres made up entirely of EPN or EPDM are still in the development stage.

The dried, anhydrous monomers ethylene and propylene and the tercomponent, the "diene", are polymerized in an inert, anhydrous solvent with the aid of Ziegler-Natta catalysts in the absence of atmospheric oxygen.

The "dienes" used are, for example, dicyclopentadiene, hexadiene-1,4, ethylidene norbornene, methyl butenyl norbornene, ect.



EPM and EPDM (Hüls-Höchst-Process)

1.41

The catalysts are mixtures of halogen-containing organic aluminum compounds and vanadium compounds.

The catalyst has a different activity on each of the three monomers. Their ratio in the polymer, therefore, is not the same as in the initial mixture of the monomers.

Alcohols and water are used for deactivating (short-stopping) the catalyst on completion of polymerization. For stabilization of EPDM use is made of the compounds customary for this purpose in the rubber industry.

1.41 Process Description (see diagram 1.41)

The anhydrous monomer feed mixture consists of

- a. the solvent (an aliphatic hydrocarbon)
- b. the liquid propylene and
- c. the ethylene dissolved under pressure in the solvent/propylene mixture
- d. the ter-monomer (a "diene" hydrocarbon) and
- e. the Ziegler-Natta mixed catalyst

This mixture is continuously introduced into the polymerization reactor, where polymerization is accomplished. The heat of polymerization is carried off by cooling.

The polymer solution is stripped of the unconverted monomers, which are recovered and recycled to the process. Then the catalyst system is destroyed by adding a short-stop; a stabilizer is added and the polymer-solution is water-washed. On separation of the water the polymer solution is coagulated by means of steam in a coagulation system and the solvent is stripped. On recovery, the solvent is prepared for reuse.

The rubber crumbs obtained in an aqueous suspension are separated from the bulk of the adherent water on a vibrating screen, the residual water being removed in a screw press or an apron dryer. Finally, the rubber is baled.

1.42 Consumption Figures

Raw Materials Required per 1 000 kg of rubber

Ethylene	490	kg
Propylene	490	kg
Diene	40	kg
Aliphatic solvent	60	kg
Chemicals	120.- to 150.-	DM

Utilities Required per 1 000 kg of rubber

Electric power (low tension)	650	kWh
Steam (20 atm)	1	MT
Steam (4 atm)	5	MT
Compressed air (5 atm)	200	Nm ³
Nitrogen (5 atm)	140	Nm ³
River water (20° C)	500	m ³

Labor Required per 1 000 kg of rubber

5 man-hours

Battery limits cost of a plant with a capacity of 20,000 MT/yr (1 line of reactors) approx. \$ 6,75 million (in the Federal Republik of Germany). This figure does not include monomer storage, finished product storage, engineering, financing, land development and lines to battery limits.

1.43 Literature

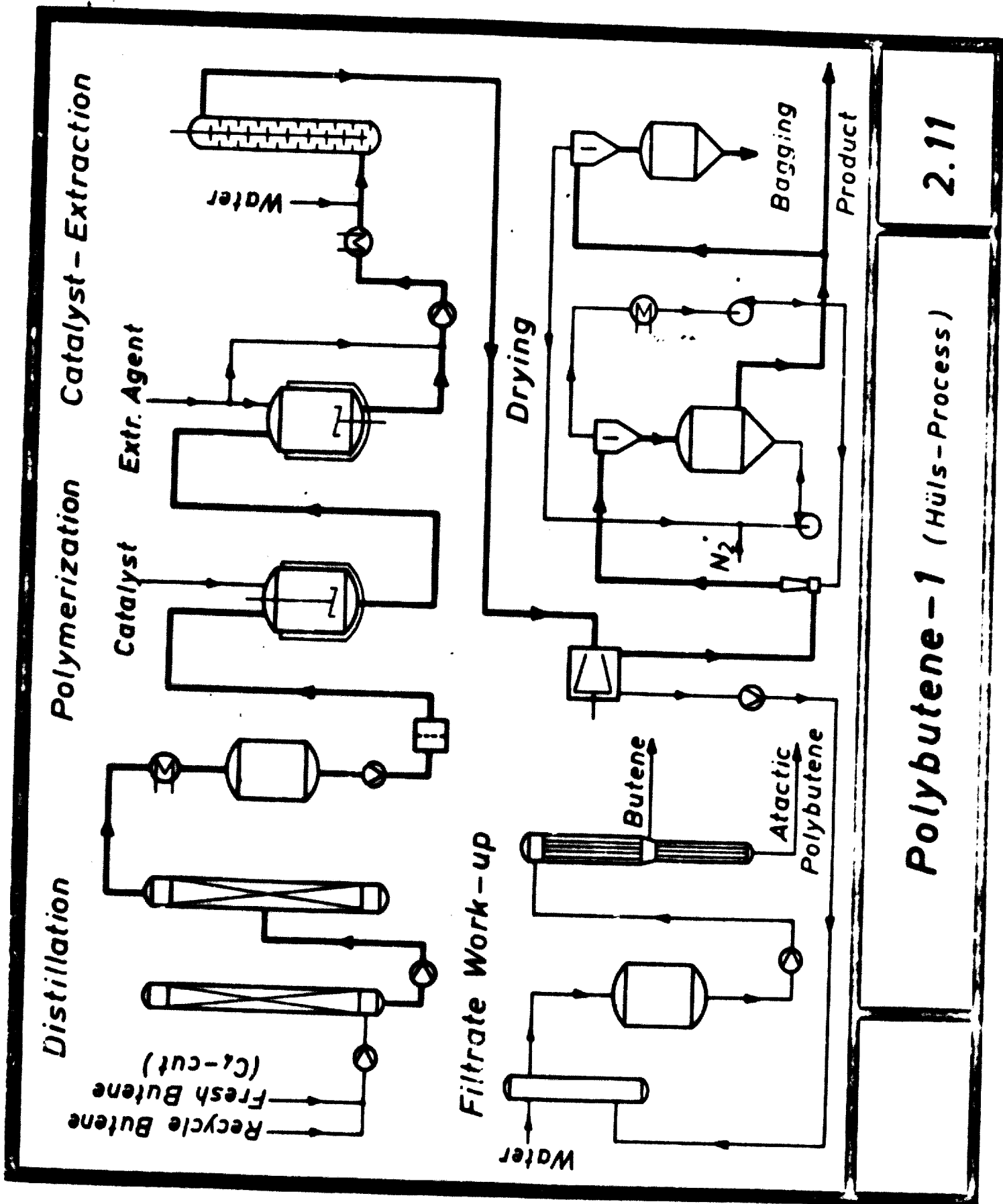
H. Blümel: Kautschuk u. Gummi, Kunststoffe
21 (1968) (10) 547

H.D. Stemmer: Kautschuk u. Gummi, Kunststoffe
21 (1968) (11) 615

2.0 Other Polymer Products

2.1 Polybuten-1 (VESTOLIN BT)

While Polybutene-1 has broken into the market only recently, it has already proved its superiority in various fields of application.



Polybutene-1 (Huls-Process)

2.11

Polybutene-1 has some essential advantages over other polyolefines (polyethylene, polypropylene) it is extremely resistant to stress cracking and exhibits lower plastic deformation under long-sustained load. An important field of application, therefore, is the pipe sector. The above-mentioned characteristics add up to outstanding internal pressure creep rupture strength compared to other polyolefines, especially also at elevated temperatures. Pipe of large diameter too can therefore be made from polybutene-1. Also, polybutene-1 lends itself remarkably well to the manufacture of pipes, vessels and pumps for handling and storing corrosive liquids, especially also under the action of pressure and temperature. At high molecular weights, too, polybutene-1 can be satisfactorily processed thermoplastically and permits application of the established methods of processing such as extrusion and injection molding.

At Hüls, Polybutene-1 is manufactured in a 1200 MT/yr. plant. A 12,000 MT/yr. plant is under construction.

Polybutene-1 is manufactured by the use of Ziegler catalysts. The feed consists of a cracked gas, which contains approx. 50% and over of n-butene-1, besides other C₄-hydrocarbons.

Water, oxygen, sulfur compounds, acetylenes and dienes must be excluded from the process.

2.11 Process Description (see diagram 2.11)

Polymerization is effected continuously. The finished product is also obtained continuously, in the form of powder.

The C₄-mixture, having passed through polymerization, can be recycled by returning it via a distillation column to polymerization. When n-butene-1 has been largely polymerized, the residual C₄-mixture can be used either for power generation or as a raw material for other processes.

The bulk of the polymer has an isotactic structure. The small proportion of atactic material can be withdrawn at the bottom of the distillation unit. It can, for example, be used for the preparation of pourable sealing compounds or other purposes.

2.12 Consumption Figures

Raw Materials Required per 1 000 kg of pellets

Hydrocarbons mixture (50 % n-buten-1 and more)	3 000	kg
Chemicals	300,-	DM

By-products per 1 000 kg of pellets

C ₄ -Hydrocarbons mixture (low in n-buten-1)	1 700	kg
Atactic polybutene-1	50	kg

Utilities Required per 1 000 kg of pellets

Electric power (low tension)	760	kWh
Electric power (6000 V)	200	kWh
Steam (20 atm)	1,2	MT
Steam (4 atm)	14	MT
Compressed air (5 atm)	1 120	Nm ³
Nitrogen (5 atm)	300	Nm ³
River water (20° C)	600	m ³
Refrigeration (-5° C)	600,000	kcal
Credit for condensate	13	MT

Labor Required for 1 000 kg pellets

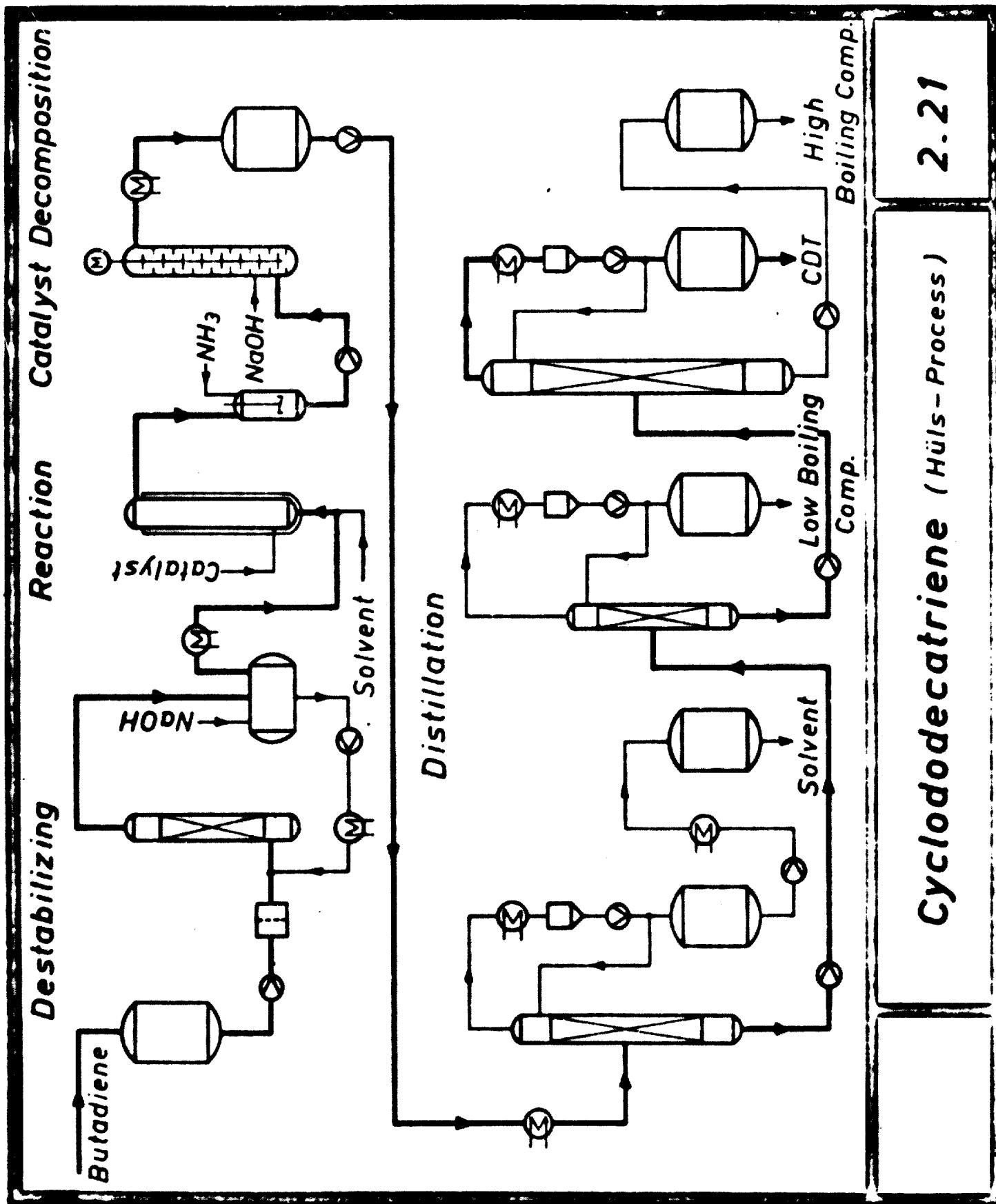
10 man-hours

Battery limits cost of a plant with a capacity of 12,000 MT/yr. Approx. \$ 5,5 million (in the Federal Republic of Germany). This figure does not cover monomer storage, finished product storage, engineering, financing, land development and lines to battery limits.

2.13 Literature

I. Plenikowski and O. Hahmann;

Chemie-Ingenieur-Technik 38 (1966) (10) 1063.

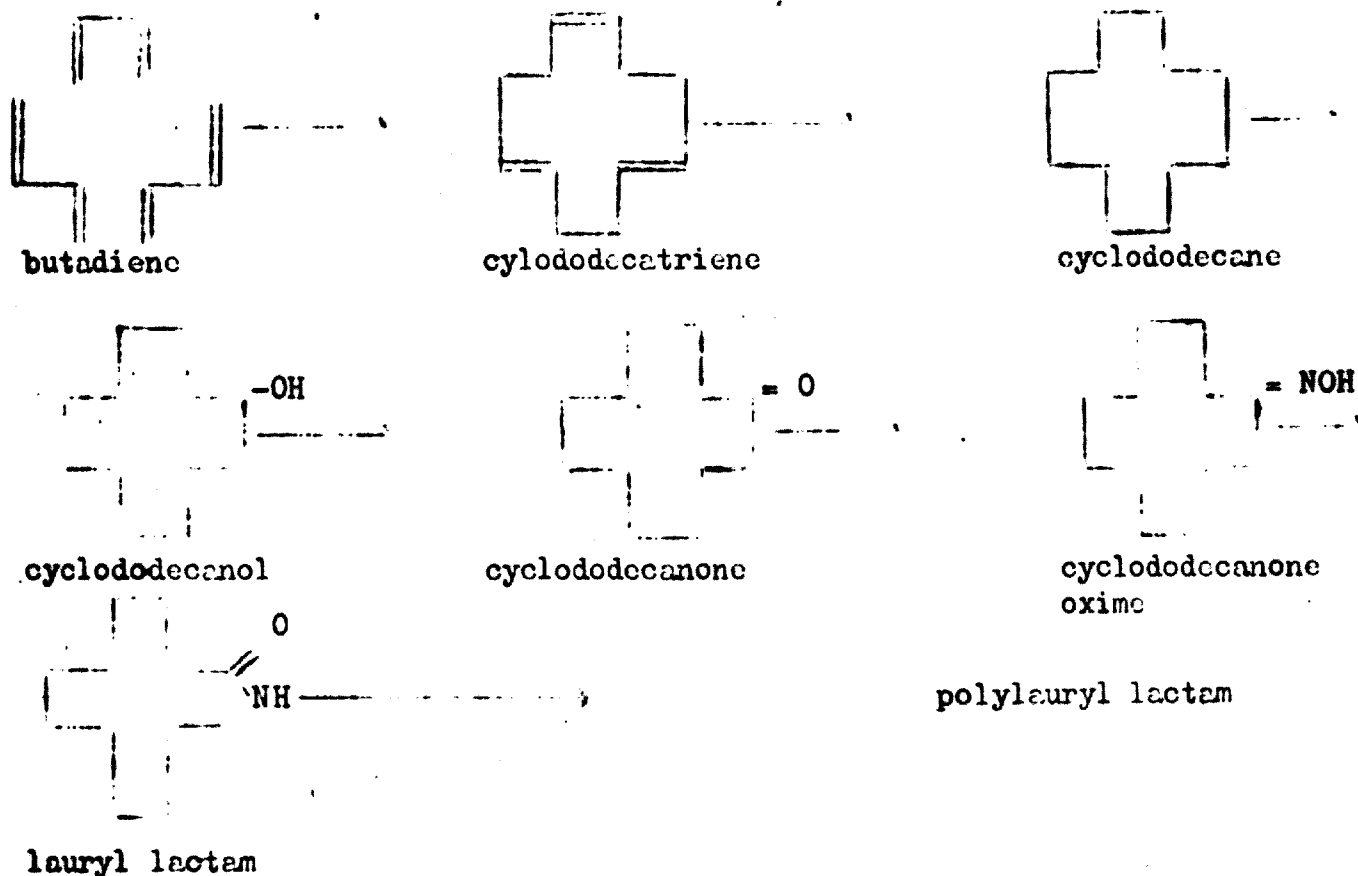


Cycloodecatriene (Hüls-Process)

2.21

2.2 Cyclododecatriene

Cyclododecatriene-1,5,9 has, in the past few years, achieved importance as a basic material for C_{12} -chemistry. At Hills, it is manufactured at a rate of 500 MT/month. This trimer of butadiene is used primarily as a starting material for the manufacture of lauryl lactam and polylauryl lactam by the following route:



Decane dicarboxylic acid is also produced from cyclododecatriene and can be used as starting material for the manufacture of polyamides and of polyesters. Hexabromocyclododecane is added as a flame retardant to the plastics.

2.21 Process Description (see diagram 2.21)

Cyclododecatriene is manufactured by trimerization of 1,3-butadiene with the aid of Ziegler catalysts in benzene at 70°C and 1 atm. absolute. On being destabilized and dried, the butadiene is heated up and in the gaseous state is introduced into the reactor. In addition, benzene and the catalyst components are fed to the process. Before initiation of the reaction, the reaction mixture is heated up and then the heat of reaction is removed using cooling water.

The product taken overhead from the reactor is treated with caustic soda solution to deactivate the catalyst, the benzene is distilled off, and the cyclododecatriene is purified by distillation. The conversion is 98%, and the yield 89%, based on the butadiene fed to the process.

2.22 Consumption Figures

Raw Materials Required per 1 000 kg of product

1,3-Butadiene	1 120	kg
Benzene	20	kg
Caustic Soda	13	kg
Chemicals	31,-	DM

By-products per 1 000 kg of product

C ₈ -Hydrocarbons	25	kg
Residue (liquid at 50° C)	70	kg

Utilities Required per 1 000 kg of product

Electric power	(low tension)	100	kWh
Steam	(20 atm)	2	MT
Steam	(4 atm)	1	MT
Compressed Air	(5 atm)	250	Nm ³
Nitrogen	(5 atm)	500	Nm ³
River water	(20° C)	400	m ³

Labor Required per 1 000 kg of product

3 man-hours

Battery limits cost of a plant with a capacity of 12,000 MT/yr. . Approx. \$ 1.25 million (in the Federal Republic of Germany). This figure does not cover monomer storage, finished product storage, engineering; financing, land development and lines to battery limits.

2.23 Literature

W.K. Franke and K.A. Müller;

Chemie-Ingenieur-Technik 36 (1964) 960.

H. Weber, W. Ring, U. Hochmuth and W.K. Franke

Liebigs Annalen der Chemie 681 (1965) 10

2.3 Polylauryl Lactam (²VESTAMID⁺)

With polylauryl lactam (polyamide 12) Hüls has in the past few years launched a new polyamide that has a number of advantages over the polyamide types previously available. So polylauryl lactam exhibits the lowest water absorption among the technical polyamides and thus has the best dimensional stability. Also, it has the lowest density, which means savings in material. Polylauryl lactam is used preferably as a material of construction for those parts which require high wear resistance and dimensional stability, such as gears, control elements for precision machinery, pneumatic dispatch carriers, etc. Polylauryl lactam has also performed well in the protection of metallic surfaces against rust and wear. For this purpose, a process for the manufacture of polylauryl lactam powder for fluidization coating has been developed and is available to Hüls.

At Hüls, polylauryl lactam is manufactured at a plant with a capacity of 2400 MT/yr.

The starting material for the manufacture of polylauryl lactam is cyclododecatricone-1,5,9 (see preceding chapter). This is hydrogenated to cyclododecane, which is then air-oxidized to a mixture of cyclododecanol and cyclododecanone. This mixture is dehydrogenated to give cyclododecanone, which is converted into cyclododecanone oxime using hydroxylamine. The oxime is rearranged to lauryl lactam with sulfuric acid. Lauryl lactam is polymerized to polylauryl lactam by hydrolysis.

2.31 Process Description (see diagram 2.31)

In a jacketed reactor, lauryl lactam is heated up and polymerized at 20 atm. gauge with the addition of an initiator. The process is a batch type operation. The reactor is emptied through spinnerets.

⁺)²VESTAMID is a product of Chemische Werke Hüls AG

The spun strands are cooled in a cooling trough and pelletized. The pellets are screened, further dried and packaged or post polymerized to give material of higher molecular weight.

2.32 Consumption Figures

Raw Materials Required for 1 000 kg of pellets

Lauryl Lactam	1 025	kg
Chemicals	4,50	DM

Utilities Required per 1 000 kg of pellets

Electric power	(low tension)	980	kWh
Steam	(20 atm)	0,9	MT
Compressed air	(5 atm)	2 000	Nm ³
Nitrogen	(5 atm)	250	Nm
River water	(20 C)	200	Nm ³

Labor Required per 1 000 kg of pellets

16 man-hours

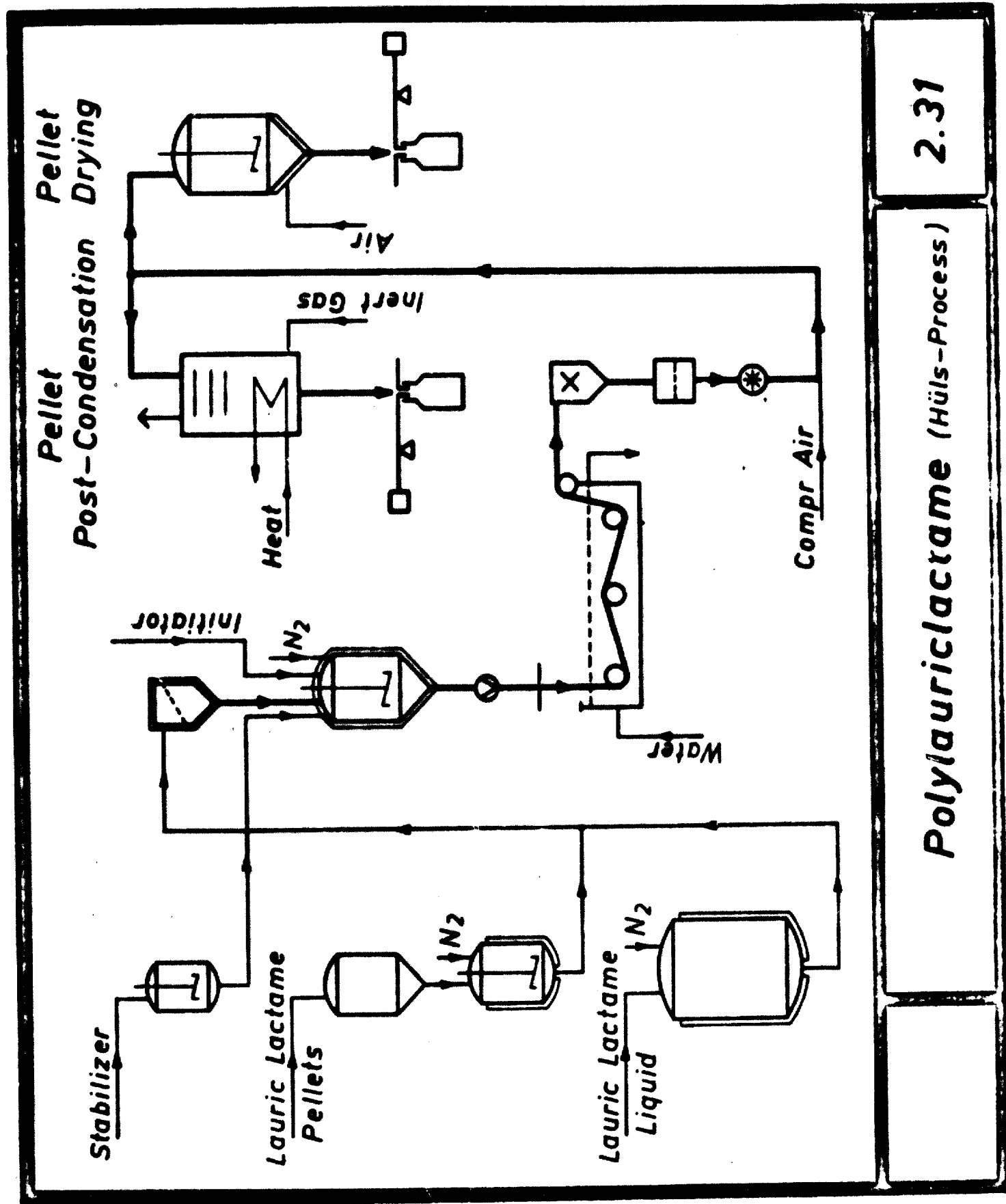
Battery limits cost of a plant with a capacity of 2400 MT/yr.

(from lactam to pellets) approx. E 0.55 million (in the Federal Republic of Germany). This figure does not cover monomer storage, finished product storage, engineering, financing, land development and lines to battery limits.

2.33 Literature

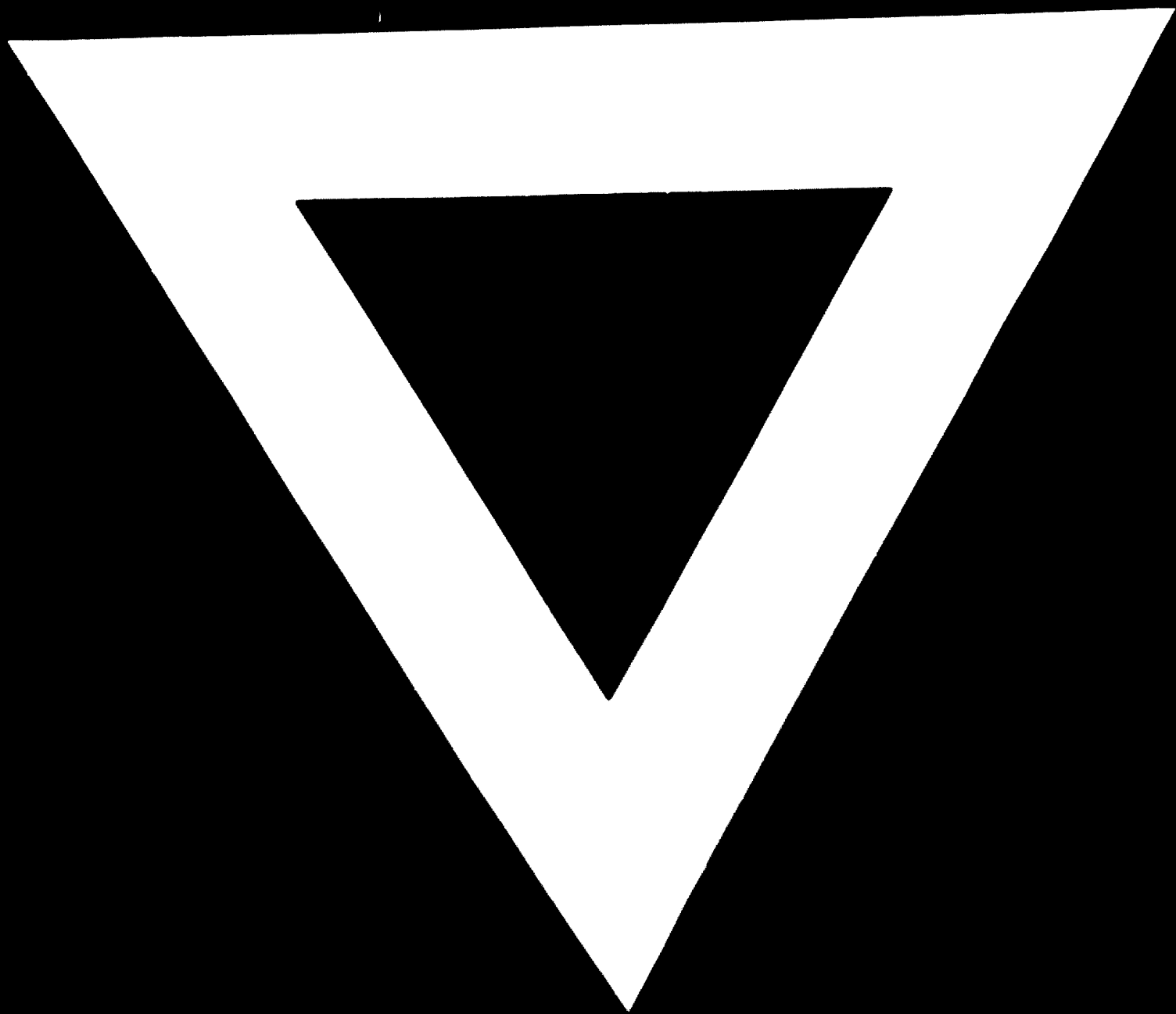
R. Kraft, Chemische Industrie 20 (1968) (11)

Except for styrene-butadiene rubber, the processes presented in this paper for the manufacture of polymer products rank with the youngest children of research and development in petrochemistry. It can be expected that these processes will gain in importance throughout the world.



Polylauric lactame (Hüls-Process)

2.31



15.

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