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REHABILITATION OF LINDANE MANUFACTURING PLANT AT DURRES

SI/ALB/88/802

SOCIALIST PEOPLE'S REPUBLIC OF ALBANIA

Technical report: Findings and recommendations*

Prepared for the Government of the Socialist People's Republic of Albania
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

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United Nations Industrial Development Organization
Vienna

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* This document has not been edited.

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1. A B S T R A C T

Consultancy of problems connected with intended rehabilitation of Lindane manufacturing plant at Durres, Albania, has been provided during the period of 1st June to 26th June 1989 on the request of the Government of Albania.
The assistance to the project authorities has been targeted mainly on assessment of the technological process and machinery with the aim to intensify the process in order to obtain higher yield and quality of the final product, to increase the capacity and to create a conception of the plant rehabilitation.

Both plants of technical BHC and of Lindane separation have been erected in cooperation with People's Republic of China that provided the licence and technological equipment in the frame of technical assistence. As the cooperation was interrupted without passing on the know-how, after a period of about 4 years the Chemical Works at Durres accomplished the erection of the plants at their own knowledge. The plants were in operation only for short periods with lack of documentation and records. The total production in 6 years has not exceeded 36 tons. According to the complex analysis the following conclusions can be drawn :

Some substantial parts of the equipment had not been supplied and some of the existing equipment have not been installed and used in accordance with the original technological conception of the licencer. Nevertheless, the rather simple process, mainly that of Lindane separation, would not have facilitated to produce pure Lindane, but a concentrate most likely of 80--90% of gamma isomer of hexachlorocyclohexane. Due to lack of regular anti-corrosive protection the machinery and equipment are generally in a critical state.

The actual machinery and equipment and know-how are not

sufficient and a serious base for a rehabilitation is intended to procure a capacity of 100 tons/year of pure Lindane. It has been recommended to purchase a complete know-how and turnkey plant. A less expensive alternative is to purchase a know-how, manufacturing equipment and basic engineering and procure the detail engineering and construction by Albanian organizations.

Several important proposals and recommendations to improve the actual technological process and machinery, to achieve higher yield and quality of the final product and intermediates, as well as suggestions to improve the analytical control and anti-corrosive protection and information on construction materials have been submitted.

The author has elaborated a conception of modified technological process of Lindane separation for the actual machinery. Its efficiency, although facilitates to obtain higher yield and quality of the final product is limited by the frame of the equipment and is to be optimized at the Research Institute of Chemistry, Tirana, according to the instructions of the author.

Estimation of construction costs for a new plant and alternatively for the plant rehabilitation have been elaborated for the decision making process.

2. INTRODUCTION

The Government of Albania has requested assistance from UNIDO to modernize their Lindane manufacturing unit at Durres and to this effect UNIDO is providing expert assistance in the field of process technology and anti-corrosion.
The author of the technical report, on one month UNIDO assignment from 30th May, 1989 to 28th June, 1989, having been briefed in Vienna by the Backstopping Officer of Chemical Industries Branch, visited the Lindane manufacturing plant at Durres, Albania, from 1st June to 26th June 1989.

The UNIDO assignment :
To provide as Process Chemist Consultant advisory services based on the existing status of the plant to :

- Take necessary measures to have smooth process flow avoiding bottlenecks;
- Take necessary measures to get a better/safer utilization of raw materials with improved quality of finished products;
- Improve the standard of the quality control laboratory;
- Provide proper training to the project personnel;
- Likely costs to rehabilitate the plant;

To submit a report on findings, recommendations and conclusions.
The objectives of the visit :

- To inspect the overall condition of the plant;
- To review and assess the machinery and equipment;
- To observe and assess the technological process in full operation;
- To study on the site all available technical documentation;
- To review records of analytical and operation control;
- To provide consultancy and pass on experience;

Conclusions, proposals and recommendations based on a complex analysis and assessment of the technology are included in the following report.

3. INSTITUTIONS VISITED AND PERSONS MET

During the period of author's mission at Durres, Albania, the following persons were met at briefings, conferences, discussions, regular working visits of the factory and Research Institute of Chemistry and informative visit of the Committee of Science and Technology :

Committee of Science and Technology :

Ilir Fico	Foreign Relations Department
Vangjush Orgocka	Specialist, Department of Technology

Ministry of Industry :

Albert Hajnaj	Director, Department of Chemistry

Chemical Works, Durres :

Adem Dizdari	Director
Prokop Biceri	Deputy director
Bebeka Dona	Chief engineer
Abdulla Myterizi	Head, Department of Technology
Andrea Koci	Head, Pesticides' Formulation Plant
Mihal Vaso	Head, Lindane Plant
Arjan Bequari	Process Chemist, Lindane Plant
Josef Zhufka	Specialist, Central Laboratory
Eduart Malltezi	Mechanic engineer
Vojsava Shtylla	Electrical enginner

Research Institute of Chemistry :

Gastor Agalliu	General director
Gazmend Gyuli	Head, Department of Organic Synthesis
Forek Borova	Head, Department of Technology
Syrja Sukaj	Head, Engineering Department
Meri Shgeri	Head, Design Department

Zamira Rada	Specialist, Department of Organic Synthesis
Figali Hila	Specialist, Department of Organic Synthesis

4. CHEMISTRY AND TECHNOLOGY IN GENERAL

Lindane is one of the oldest synthetic pesticides and has been used in the fields of pest control, crop protection, forestry, seed treatment, timber protection, public health and veterinary hygiene for more than forty years. Lindane is offered in numerous formulations, the most important of which are wettable powders, emulsion concentrates, suspensions and powders but also solutions, dusts, granules, baits, preparations for fumigations, aerosols and special formulations are produced. Because of its versatility, low toxicity, stability and compatibility when mixed with other biologically active substances, Lindane is often used in mixed formulations with other insecticides and fungicides.
By virtue of its chemical structure and biological properties, Lindane holds a unique place among chlorinated hydrocarbon insecticides and though restricted in several countries it has still preserved adequate relevance in worldwide pesticides production and plant protection systems.

Benzene hexachloride is normally produced by simple additive chlorination of benzene in presence of light as catalyst. The industrially applied processes of photochemical reaction of gaseous chlorine with benzene, mostly operated continuously, differ in varying conditions (temperature , concentrations, catalyst) and the mechanical equipment. Products manufactured accordingly to such processes contain a mixture of stereo isomers accompanied by small proportions of higher chlorinated compounds as isomers of heptachlorocyclohexane and isomers of octachlorocyclohexane. Of these various components of the crude reaction mixture only the gamma isomer, which is formed in minor proportion, is a valuable insecticide, the other components being relatively valueless, except as chemical intermediates. Accordingly, many processes have been devised for separating the gamma isomer from the accompanying unwanted isomers and impurities and a simple and efficient method of carrying out the separation is an important industrial objective.

Theoretically BHC can exist as 17 optical or stereo isomers. However spatial and energy system considerations show that only 9 of these isomers are possible. The alpha, beta, gamma, delta, epsilon and zeta isomers of hexachlorocyclohexane result from the chlorination of benzene and are present in technical BHC in considerable quantities. All isomers of hexachlorocyclohexane, heptachlorocyclohexane and octachlorocyclohexane differ in their physical properties. In technical BHC, the gamma isomer is present to the extent from 12% to 15%, while the alpha isomer represents about 60% of the total chlorination product. In the most of the wellknown solvents the gamma isomer is from 2 to 4 times as soluble as the alpha isomer and a number of processes for isolating the gamma isomer have been based on this fact.

The industrial production of Lindane is effected according to various technological processes but generally the technical BHC is extracted with a limited amount of the selected organic solvent so that practically all the gamma isomer dissolves but only a comparatively small proportion of the alpha isomer. Isolation of pure gamma isomer is achieved by several subsequent fractional crystallizations of supersaturated solutions. Due to numerous different operations, intricate disposal of liquors and recovery system of solvents, the technological processes operated exclusively batchwise are rather complicated and exacting.

As the content of gamma isomer varying in technical BHC in the range from 12% to 15% is relatively low and several solid wastes with considerable content of gamma isomer are inevitable, the optimum yields obtainable, applying economically feasible system of processes and operations, does not exceed 8-9%.

5. LINDANE MANUFACTURING PROCESS AT THE CHEMICAL WORKS, DURRES

Only a short informative outline is presented, as a complex analysis is the objective of the next chapter. A block diagram illustrating the technological process has been elaborated; see Annexe 1 and 2. All processes are operated batchwise.

The photochemical reaction of benzene is carried out in 2 reactors of 1200 l volume and 6 reactors of 600 l volume at the range of temperatures from 45°C to 55°C during 3 hours. Caissons with liquid chlorine are placed on weighs; chlorine evaporated in heat exchangers is led to the bottom of the reactors. Excessive chlorine from reactors is absorbed in benzene in 2 absorbers of 2000 l volume. The hydrogen chloride is absorbed in column by 15% solution of natrium hydroxide. Crude reaction mixture containing 30% of BHC is washed with water, neutralized by 5% solution of natrium hyposulphite and 2.5% solution of natrium carbonate in a reactor of 2000 l volume. In 2 distillation apparatuses of 2000 l volume is benzene distilled off at the temperature from 78°C to 107°C, condensed and cooled in 2 heat exchangers and after water separation charged with fresh benzene into the process again. Melted BHC is granulated in water and after some days of free storing dried by direct hot air in a drying system.

Technical BHC is ground, milled and together with extraction mixture charged into 4 extractors. The ratio of technical BHC and extraction mixture is approximately 1 : 4.25 varying accordingly to the specific gravity; the extraction is carried out at 40°C in 1.5 hours. The extract separated from undissolved unwanted isomers in a chamber filter press is charged into 4 crystallizers of 2000l volume, where it is cooled down to 15°C. The final product is separated on a pendulum centrifuge, while the mother liquor is added together with fresh methanol to the extraction mixture. The filter cake from chamber filter press is the only one solid waste.

6. COMPLEX ANALYSIS AND ASSESSMENT OF THE TECHNOLOGY

The analysis and assessment is based on a study of technical documentation and operation records in very limited scope, review and inspection of the machinery and equipment, and observation of the technological process. Though the management of the plant has made a serious effort to set the process in full operation, due to the poor state of machinery, several breakdowns, impurities in the benzene and some problems with steam supplies, only a small quantity of 45 kg of gamma isomer concentrate has been produced. During the author's stay 15 operations of chlorination, 8 operations of neutralization and distillation, 4 operations of granulation (without drying), 6 operations of extraction and filtration and 4 operations of crystallization and separation have been made. Mainly in the section of Lindane separation has not been achieved a stationary state and equilibrium of mother liquors and extraction mixture. However, a certain image of the whole technology has been illustrated.

6.1. Raw materials and chemicals

The following raw materials and chemicals are used at the manufacturing process : chlorine, benzene, caustic soda, natrium hyposulfite, methanol, nitrogen. The qualitative parameters of all raw materials correspond to international standards (ISO) and fulfill the requirements of the technological process.

6.2. Intermediates

Due to simplified process of Lindane separation only one separated and defined intermediate, the technical benzenehexachloride is produced. Available analytical data of one longer period of operation from 23/7/1988 to 8/9/1988 have shown that the content of gamma isomer HCH varies in the range from 10.5% to 14.5%, with average of 12.1%, while 11 samples of 24 have contained less than 12%. The gamma isomer content of 12% can be considered as the lowest limit for economically acceptable Lindane separation. The relatively large range of gamma isomer content indicates deviations in the technological regime or in analytical procedure. The true reason can not be detected as no periodical technological reports have been made.

The content of volatile matters does not exceed 0.6% and is relatively low considering the simple construction of drying system and its expectable efficiency.

The very low acidity of the product, less than 0.01% bears out the efficiency of the washing and neutralization processes.

Other qualitative parameters, as the content of unwanted isomers and the content of water have not been determined.

The product of white-gray colour is solid and well grindable.

Conclusion : The product of some operation periods, although of low gamma isomer content, is suitable for Lindane separation.

6.3. Final product

Analytical data of the period from 25/7/1988 to 8/9/1988 have shown that a gamma isomer concentrate with average content of 98.1% has been produced in the first 11 operation cycles and later as an equilibrium of mother liquors and extraction mixture has been achieved, the average content has lessend to 71.8%. At random taken 3 samples of stored product have contained 58.8, 73.6 and 72.4% of gamma isomer HCH. The mat appearance and gray shade of the product is not characteristic for Lindane.

The method of melting point determination is not introduced.

Conclusion : The simple technological process of isolation does not allow to obtain pure Lindane identical to the AFNOR-

ISO and WHO definition, i.e. 99.0% content of gamma isomer HCH in the product with melting point of 112.8°C.

6.4. Wastes

Water solution from the alkaline absorbtion of hydrochloric acid containing 15-20% of natrium chloride and natrium hypochlorite, waters from washing, neutralization and granulation are freely discharged into the drains. No disposals and records of quantities and composition.
Solid waste from the filtration containing mainly alpha and beta isomers is stored provisionally without disposal. The content of gamma isomer HCH in the period from 23/7/1988 to 8/9/1988 has varied in the range 1.1 - 3.9% with the average content 2.4%, which is rather high.

Conclusion : In the presence of organic matters (e.g. benzene) the neutralization process in the absorbtion column may be followed by an oxidation reaction even of an explosive character at higher temperatures. Temperature registration and automatic safety valve on the inlet pipe into the absorbtion column is recommendable.
For economical Lindane manufacturing is necessary to ensure a steady efficiency of extraction process giving less than 1.0% content of gamma isomer HCH in the solid waste. The high content of gamma isomer is due either to improper ratio of extract solution and charged technical BHC or great difference between the temperatures of extraction solution and filtrate.

6.5. Technological process

Owing to the complicated technology, only the most important problems are discussed in a concise form. Elaborated block diagrams, see Annexes 1 and 2, are illustrative of processes and operations. All processes in both techn. BHC and Lindane plants are operated batchwise, which limitates the regime of chlorination, but offers a lot of advantages in the other technological stages. The actual process of chlorination is very simple from the operational point of view but the low volume of reactors does not allow to work with lower content of BHC in the crude reaction mixture. For optimal yield of gamma isomer has been pointed out to operate in the range of 15-20% of BHC content.

The path of gaseous chlorine in the reactor is short, so a great part of the chlorine is not able to react and procede immediately to the absorbtion. In case of lower dosing the reaction time prolongs. The recommended temperature for benzene chlorination is 45-50°C, while the first stage of dissolving the chlorine in the benzene is enabled by lower temperature under 30°C and the end of reaction by elevating the temperature to 70°C. It is reasonable to keep the temperature of evaporated chlorine under 20°C, otherwise the solubility in benzene is low. Actually, there is no temperature control of the evaporation of chlorine.

The present system of chlorine absorbtion is ineffective due to inconvenient construction of the equipement.

The absorbtion of hydrochloric acid ought to be controled by an automatic safety system including temperature registration and signalization; see Section 6.4 . The waste waters may be treated on hydrated lime in a vat.

The washing and both neutralization processes are efficient. Elevation of the temperature in the last phase of the chlorination will facilitate the neutralization. At the preparation of neutralization solutions is necessary to prevent any contamination working in rusty essels.

The distillation process carried out in one step is not completely mastered and there is no control of the end of the operation. As a result, product with high content of monochlorobenzene and dichlorobenzene can be discharged. In analogous technologies the distillation is usually operated in 3 steps.

The granulation and drying processes, being only improvised, do not respond to the basic requirements as far as the safety of operation is concerned. Neither do they facilitate acceptable hygienic working conditions.

The technical BHC grinding and milling is well operated.

The charging of technical BHC into the extraction is not mechanized and requires a lot of manual work and effort.

The process of extraction is not effective to the full as a great quantity of mother liquors is circulated. The ratio of extraction mixture and technical BHC is not optimal and can be lessend. Neither does it consider the composition of the extraction mixture. On the whole, the process does not ensure a steady 1.5% or less content of gamma isomer in the solid waste.

The operation time of unwanted isomers separation is too long and possibly a gamma isomer crystallization may occur, lowering the yield of final product. The high content of methanol in the filter cake increases the consumption figures and production costs.

The only one crystallization process completed invariably at 15°C does not allow to produce pure Lindane for a longer period of operation, but a rich concentrate containing 80-90% of gamma isomer HCH.

Anyhow, there is no real knowledge how to perform the crystallization of Lindane, as every one operation is individual due to different compositions of batches and critical crystallization temperatures that ought to be determined.

The Lindane and mother liquor can be separated by centrifugation, just the existing equipment is not the most suitable for this purpose, see Section 6.6.

For a successful and steady Lindane manufacturing is necessary to remove all unwanted isomers of the system. At the present state the quantity of mother liquors rises in every cycle and in consequence the extraction mixture is supersaturated by delta and epsilon isomers of HCH, isomers of heptaclorocyclohexane and octachlorocyclohexane.

A certain quantity of water is accumulated in the circulating methanol that hinders the effectiveness of the extraction. The water is to be removed by a methanol recovery system.

All processes in both plants are operated manually, which is adequate to the relatively low capacity, as mainly in Lindane plant up to a capacity of 500 t/year the regime is not stationary enough for a full automatic remote control and partial applications do not offer any economic advantage.

Conclusion : The actual technology is not complete and sufficient for Lindane manufacturing and is a serious case for rehabilitation.

6.6. Process machinery and equipment

Both basic and detail engineering including design details have been provided by Chemical Works, Durres. As not a complete know-how had the Chinese licencer passed on, many parts of the machinery are improvised, the choice of others not being the most appropriate.

The equipment for chlorine evaporation is based on a simple spiral tube exchanger heated by direct steam, which is not acceptable. There is no temperature control in tne whole system up to chlorination reactors, so overheated chlorine may get into reactors. The chlorine distribution piping system and armature is rather complicated; the size of chlorine valves is not dimensioned proportionally. There is no absorbtion and neutralization equipment in the store to use in the case of a heavy breakdown on the system and intensive chlorine emission. The batchwise operation of the benzene chlorination allows to operate without flowmeters as the quantities of both raw materials are measured differentially, though the instruments ought to be at disposal.

The design of the chlorination reactors, mainly volume, shape and chlorine inlet are not characteristic and optimum for this type of reaction. The path of chlorine is short and distribution unsufficient. The light installation for photochemical catalysis is in a critical state, unfit for use.

The absorbers of chlorine are not of suitable type and efficient enough. The equipment for hydrochloric acid absorbtion

is not complete, see Section 6.4. and 6.5.
The distillation equipment does not allow to perform the operation in three stages as it would be advantageous and there is no control of the process except a thermometer. The condensers are situated too far from the apparatuses.
The granulation is carried out in a simple uncovered vat without agitation. The drying equipment consists of several steel chambers with perfored bottom plates on which the product is dried with direct hot air forced through by means of centrifugal fans. Both these equipment do not fulfill safety labour and hygienic requirements.
The mill suits for technical BHC grinding and is in a good state.
Enamelled extractors and crystallizers are of standard types and suitable for the processes. The inappropriate high degree of corrosion indicates a second rate quality supply and possible misshandling during the transport and assembly.
There is no equipment for technical BHC charging into extraction which calls for a higher ratio of manual labour.
The chamber filter press is of standard performance but not the most convenient for unwanted isomers separation, where low methanol content in filter cake is required.
The pendulum centrifuge is a valuable equipment suitable for gamma isomer concentrate separation. For the separation of Lindane itself a type with upper discharging of the whole charge would be more convenient to prevent that any rest on the filter cloth could diminish the quality of the next batch
The distillation columns have not been equipped with condensors.
There is no methanol recovery equipment in the plant.
The piping system and armature including instrumentals are not of desirable level at full extent of the plant.
The brine cooling station is well designed with high reserve in performance and is in a good state.

Conclusion : The machinery and equipment in general are in a bad state due to lack of regular and qualified preventive maintenance and anti-corrosive protection. The high rate of corrosion in a great deal is caused by improper choice of construction materials. In author's opinion some of the supplied enamelled reactors and armature have not been of guaranteed first class quality. The process machinery is incomplete and improvised in some technological steps. Mainly the granulation and drying equipment do not offer acceptable conditions as the hygiene and labour safety are concerned.

To all intents and purposes the equipment except the mill, centrifuge and brine cooling station does not virtually represent a great technical value and is a dubious base for a rehabilitation of a larger scale. Considering the conclusions of previous section the present technology can not be conceived as a complete and reliable know-how for Lindane manufacturing, rehabilitation of the plant or construction of a new plant.

6.7. Analytical control

Complete set of analytical methods for the determination of all qualitative parameters of raw materials is available at the Research Institute of Chemistry, Tirana. A periodical control is performed as the quality of raw materials guaranteed by suppliers does not vary. At random the content of water in benzene is determined at the institute and the acidity of methanol at the central laboratory.

The operation in the plant of BHC and the quality of intermediates is controled regularly. The following parameters of every batch are determined :

- Content of HCH in crude reaction mixture
- Content of free chlorine and acidity of the washed reaction mixture
- Specific gravity of the crude reaction mixture
- Content of chlorine and acidity of the washed reaction mixture

- Acidity of the waste water of washing operation
- Content of free chlorine and acidity of the neutralized reaction
- Content of 5 isomers in the technical BHC, mainly gamma isomer HCH
- Content of volatile matters

In the plant of Lindane separation the following parameters are determined :
- Specific gravity of the extraction mixture
- Content of gamma isomer HCH in the solid waste
- Content of methanol in the solid waste

For a certain period of operation had been determined :
- Content of gamma isomer HCH in extraction mixture
- Content of gamma isomer HCH in the extract
- Specific gravity of the extract

Lindane as a final product is regularly sampled and analysed. The content of gamma isomer HCH in each charge is determined.

Conclusion : The scope of the analytical control in general is sufficient. Owing to the fact that standards for the gas chromatography are not available, only the determination of gamma isomer HCH in technical BCH and intermediates is exact, the content of other isomers being an approximate estimation. Recommendations see Chapter 8, Section 8.3.

6.8. Operation factors

The analysis of major operation factors has been constrained by the lack of systematic operation and analytical records and incomplete documentation.

6.8.1. Annual operation hours

The high rate of corrosion, different construction materials of the machinery and equipment and a rather complicated and exacting technological process call for a well planned and predicted preventive maintenance and perfect anti-corrosive protection. Regular 2-day intervals for preventive maintenance and repairs ought to be included and scheduled in the operation plan each month and a shut down for a general repair of 30 days each year. Consequently, the annual fund of 7200 operation hours, or 300 days respectively, is to be taken into consideration for capacity calculation.

6.8.2. Annual production capacity

The important operations and parts of the machinery considering the plant capacity are :

- Chlorination
- Distillation
- Extraction
- Filtration
- Crystallization
- Separation of Lindane

Other less decisive operations and equipment as chlorine evaporation, chlorine absorbtion, hydrochloric acid absorbtion, washing and neutralization, granulation and drying have not substantial influence on the plant capacity being adequatly and proportionally dimensioned.

Chlorination is supposed to be carried out in two reactors of 1200 l volume (No 7 and No 8) and 6 reactors of 600 l volume (No 1 to No 6).

Operation time :	Charging	30 min
	Chlorination	180 min
	Discharging	15 min
	Reserve	15 min
	Total	240 min = 4 hod

Number of operations in reactors No 7 and No 8 per shift	4
Number of operations per day	12

Yield of 1 operation in reactors No 7 and No 8 :

	Volume of benzene	0.800 m^3
	Weight of benzene	0.704 t
	Weight of chlorine	0.180 t
	Weight of CRM	0.884 t
	Content of BHC (≐20%)	0.174 t
Yield of 12 operations		2.112 t/day

Annual maximum capacity of reactors No 7 and No 8 :
633.6 t/year

Number of operations in reactor No 1 to No 6 per shift		12
Number of operations per day		36

Yield of 1 operation in reactors No 1 to No 6 :

	Volume of benzene	0.450 m^3
	Weight of benzene	0.396 t
	Weight of chlorine	0.090 t
	Weight of CRM	0.486 t
	Content of BHC (≐20%)	0.097 t
Yield of 36 operations		3.492 t/day

Annual maximum capacity of reactors No 1 to No6 :
1047.6 t/year

Maximum capacity of chlorination 1681.2 t/year

Considering a real consumption of 14 t of BHC for the separation of 1 t of Lindane, the maximum capacity of chlorination corresponds to an annual production of 120 t of Lindane. In fact a parallel operation of 8 reactors is not realistic and the individual volume of small reactors (600 l) is not rational for the relatively complicated process. So only the capacity of reactors No 7 and No 8 is from technical point of view reasonable. The maximum capacity of reactors No 7 and No 8, which is 633 t/year, corresponds to an annual production of 45 t of Lindane. According to the author's opinion and experience a production of BHC corresponding to 30 t/year of Lindane can be considered as real annual capacity of chlorination at the being state of machinery, maintenance and working team's ability.

Distillation is carried out in two vessels of 1200 l volume.

Operation time :	Charging	30 min
	Warming up	30 min
	Distillation	120 min
	Discharging	210 min =
		= 3 hours 30 min

Number of operations per shift	4
Number of operations per day	12

The charge of one operation represents 1600 l of crude reaction mixture containing 20% of BHC, which responds to 0.352 t

The yield of 12 operations	4.224 t
Annual maximum capacity	1267.2 t/year
Corresponding annual Lindane production	90.5 t/year

Extraction is performed in 4 extractors of 2000 l volume.

Operation time :	Charging and warming up	30 min
	Extraction	120 min
	Discharging	60 min
	Reserve	30 min
	Total	240 min =
		= 4 hours

Number of operations per shift	6
Number of operations per day	24
Charge of BHC into 1 operation	0.400 t
Charge of BHC into 24 operations	9.600 t
Annual amount of extracted BHC, maximum capacity	2880.0 t/year
Corresponding annual Lindane production	205.0 t/year

Filtration process is provided by one chamber filter press.

Operation time :	Charging and filtration	60 min
	Discharging	150 min
	Reserve	30 min
	Total	240 min =
		= 4 hours

Number of operations per shift	2
Number of operations per day	6
Amount of extracted BHC for 1 operation	0.6 t
Amount of extracted BHC for 6 operations	3.6 t
Annual amount of extracted BHC	1080.0 t/year
Corresponding annual Lindane production	77.1 t/year

Crystallization is carried out in 4 crystallizers of 2000 l volume.

Operation time :	Charging	60 min
	Cooling	90 min
	Discharging	30 min
	Total	180 min =
		= 3 hours

At present the discharging time of the crystalizer is 60 min due to long separation in the centrifuge, caused probably by inconvenient filter cloth. In normal conditions the charging of the centrifuge must be carried out in 15-30 min, as it is considered above.

Number of operations per shift	8
Number of operations per day	24

Charge of 1 operation equals 0.4 t of BHC, it means 0.028 t of Lindane

Charge of 24 operations	0.672 t/day
Annual maximum capacity	201.6 t/year

Note : 0.028 t of Lindane represents a 7% yield from technical BHC containing 12% of gamma isomer HCH.

Separation on pendulum centrifuge, D = 940 mm
h = 400 mm

Operation time :	Charging	60 min
	Discharging	30 min
	Reserve	30 min
	Total	120 min =
		= 4 hours
Number of operations per shift		4
Number of operations per day		12
Charge of 1 operation		0.028 t
Charge of 12 operations		0.336 t
Annual maximum capacity		100.8 t/year

Note : A more suitable filter cloth would facilitate a higher capacity of the equipment and of the crystallization process as well.

Conclusion : Operation and equipment of chlorination have the lowest capacity corresponding to the annual production of 30 t of Lindane. The capacity of distillation corresponds to 90 t/year of Lindane and the capacity of filtration to 77 t/year. As at the present time the equipment of chlorination is the bottleneck of a plant, the maximum effective capacity of the whole plant is 30 t of Lindane in a year, providing an adequat preventive maintenance with required spare parts and systematic anti-corrosive protection.
A local dearation installed to the chamber filter press would allow to shorten the time of discharging and reach the full capacity of the operation.
The relatively high capacity of extraction and crystallization enable to use 2 or 3 reactors for other crystallization processes if modified technology is to be used.
Nevertheless, conclusions arrived at in Chapter 6, Section 6.7 are to be kept in mind.

6.8.3. Consumption figures

Construction of the plant was finished in the year of 1984 and start-up took place in the month of October.

Outline of annual production is following :

BHC techn.	Plan [t]	Production [t]
1984	530	no records
1985	1650	319
1986	1650	272
1987	640	125
1988	265	8
1989	265	0

Lindane	Plan [t]	Production [t]
1984	50	3.56
1985	150	14.43
1986	100	12.25
1987	60	2.77
1988	25	2.00
1989	25	1.00

Project consumption figures :

BHC techn.	Chlorine	0.790	t/t
	Benzene	0.672	t/t
	Caustic soda	0.500	t/t
	Nitrogen	0.150	t/t
	Steam	3	t/t
	Water	50	m^3/t
	Electric power	170	kWh/t
Lindane	BHC techn.	11000	t/t;
		13000	t/t from 1988
	Methanol	2000	t/t
	Steam	4	t/t
	Electric power	2000	kWh/t

Factual consumption figures :

BHC techn.		1985	1986	1987
Chlorine	[t/t]	0.761	0.796	0.790
Benzene	[t/t]	0.779	0.686	0.693
Caustic soda	[t/t]	0.511	0.417	0.642
Nitrogen	[t/t]	1.365	0.150	-
Steam	[t/t]	0.312	-	-
Electric power	[kWh/t]	0.376	0.304	0.256

Lindane		1985	1986	1987
BHC techn.	[t/t]	9840.60	10557.06	901.44
Methanol	[t/t]	3028.41	2878.12	3348.01
Steam	[t/t]	0.51	-	-
Electric power	[kWh/t]	2066.80	3778.61	1638.98

Conclusion : The available data are incomplete and the powers are not measured exactly. The factual consumption of raw materials for the production of BHC techn. corresponds to the project. Nevertheless, the consumption figures of benzene, both planned and factual are rather high.

The project consumption figures of raw materials for Lindane separation are underestimated and do not correspond to the content of gamma isomer (12-13%) in BHC techn. They neither enable to produce pure Lindane. The low figures of factual consumption indicate that either the records or weighing are not correct or the product was only a concentrate containing no more than 75% of gamma isomer HCH. As no analytical data are available of those operation periods, it is not possible to assess the true reason of disproportion.

For the first period of production the following consumption figures are recommended

BHC techn.:	Chlorine	0.790 t/t
	Benzene	0.550 t/t
Lindane :	BHC techn.	14000 t/t
	Methanol	4500 t/t

It is necessary to ensure exact weighing of raw materials and final product, regular and detailed recording and periodical evaluation of material balance in accordance with analytical data.

6.8.4. Labour requirement for plant operation

Successful operation in BHC and Lindane plants depends on high degree on the experience of operators, their initiative and working discipline. As the plants were not in full operation, the working team was not complete. Also the numerous break downs hindered a smooth and good performance. In spite of that, according to author's opinion a competent working team is possible to set up, providing a properly organized schooling. The plant management is aware of some reserves in manpower, therefore a simple systemization suggestion without comment is joined. At the present state the operation is organized in 3 shifts. A non-stop operation in 4 shifts has been recommended.

Profession/Operation	Number	
Technical personnel	Project *)	Suggestion **)
- Head of the plant	1	1
- Process chemist	1	1
- Shift engineer	3	4
- Laboratory assistent	6	6
- Mechanical engineer	-	1
- Electrical engineer	-	1
Daily workers		
- Operator/Reserve	-	5
Shift workers		
- Forman	3	4

- Operator/Stor	3	1
- Operator/Chlorine evaporation	6	4
- Operator/Chlorination	9	4
- Operator/Benzene distillation	6	4
- Operator/RM-washing	6	4
- Operator/Drying	2	4
- Operator/Transport	2	-
- Operator/Milling	2	4
- Operator/BHC packing	2	2
- Operator/Extraction and crystallization	6	8
- Operator/Methanol distillation	4	4
- Operator/Separation	3	4
- Operator/Waste drying	3	-
- Operator/Filter press discharging	3	4
- Operator/Lindane packing	3	-
Total	= 74	70

*) 3-shift operation

**) 4-shift operation

7. EXPERIMENTAL WORK

After a thorough technical auditing and assessment of the technology the author came to the conclusion that actual process does not allow to produce Lindane for long run periods. The experimental work should have found out whether a modification of the process were conceivable. The experimental work carried out at the Reaserch Institute in Tirana (40 km distant from Durres) in limited time is only of informative character :

The aim of the first set of experiments was to find out whether it is possible to obtain Lindane from the concentrate produced at the plant. Three charges of the product were sampled and the content of gamma isomer by gas chromatography was determined. The results showed that the products were of low quality :

Sample No 1	58.8%
Sample No 2	73.6%
Sample No 3	72.4%

Recrystallization of these samples with 350 ml, 300 ml and 250 ml of methanol and 100 g of the concentrates proved the possibility to obtain products of higher quality, as results were :

Sample No 1	94.5% ;	31 g
Sample No 2	98.2% ;	54 g
Sample No 3	98.6% ;	52 g

In the second set of experiments the laboratory equipement was tested,mainly the effiency of extration, the shape and the revolution of the agitator and a certain experience of the staff has been gained.

The fractional crystallization of the extract and elimination of the unwanted isomers have been studied in the third set of experiments. It has been proved that it is possible to obtain subsequently two gamma isomer concentrates of the extract. The first with a content of 70-85% of gamma isomer HCH and the second with a content of 30-45% . The unwanted isomers where eliminated by distilling off the methanol from the last mother liquor. As the content of gamma isomer in the residue was below 18% , the crystallization processes were efficient. Limited time did not allow to find out the optimum conditions of extraction and crystallization processes as 4-6 cycles are necessary for an equilibrium of extraction mixture, extract and mother liquors. Instructions for further experimental work have been left at the institute.

8. PROPOSALS AND RECOMMENDATIONS

The author used the everyday occasions at the routine inspections of the plant to hand over a knowledge and discuss the most important problems in detail. At several meetings, mainly at the final session at Research Institute of Chemistry, recommendations and proposals for process and machinery improvements have been passed on. An outline in concise form is given in the following sections.

8.1. Technological process

For an optimum regime of the chlorination is recommendable to operate in three stages. In the first stage the gaseous chlorine ought to be dissolved in benzene, therefore a temperature of inlet chlorine under 20°C is to be ensured. The relatively highest yield of gamma isomer HCH is obtained in the temperature range from 40°C to 50°C at which the second and essential stage of chlorination is to be carried out. In the third stage the free chlorine in the reaction mixture is forced to react at a temperature between 65° and 75°C for 15-30 min. The proportion of gamma isomer formed in the process can be increased when operating in the range of BHC content in the crude reaction mixture from 15% to 20%. At the end of a properly operated chlorination the reaction mixture ought to be colourless and clear.

It is advantageous to absorb the excessive chlorine of the reactors in continuously circulating benzene providing a high interphase surface, e.g. on rashing rings in a glass absorbtion column. The absorbtion benzene is then charged into the next chlorination.

It has been recommended to operate the distillation in two steps, which allows to distill off approximately 20% of benzene in the first step. In case that the chlorination has not been carried out properly and/or in the presence of iron

ionts or other impurities catalyzing substitution chlorination the formed hydrogen chloride is removed at this step.
It is necessary to introduce a regulated granulation process, in order to obtain well defined granules under 4 mm of diameter, and water separation process.
The waste waters of BHC plant can be treated on hydrated lime.
Efficient extraction is a prerequisite for high yields of Lindane. Is is necessary to determine the optimum quantity of extraction mixture and its dependence on the content of mother liquor or specific gravity respectively as the simplest characteristic. The actual ratio of 1700 l of extraction mixture to 400 kg of BHC is in author's opinion high and can be lessen substantially. That would allow to intensify the process and charge into one operation 1400-1600 l of extraction mixture and 500 kg of BHC. It is necessary to ensure the minimum temperature difference of inlet and outlet extract on the chamber filter press in order to hinder the gamma isomer crystallization. Both these measures will facilitate a less than 1.0% gamma isomer content in the solid waste, that is required for a yield of final product above 7% and economical Lindane manufacturing.
A modification of the technology including above mentioned recommendations and three additional processes has been elaborated and suggested. In order to obtain regularly pure Lindane, it is necessary to perform a recrystallization of gamma isomer concentrate dissolving it in methanol at the boilling point. The required quantity of methanol and critical crystallization temperature is to be determined for every batch according to the method given in Section 8.3. The equipment has to be clean, the critical crystallization temperature must not be surpassed and operation of separation is to be carried out as quickly as possible.
In order to elevate the yield of gamma isomer HCH a further crystallization of mother liquors from the first crystallization at the temperature in the range from -5°C to 4°C has

been suggested. The crystalline product separated by centrifugation will contain 30-45% of gamma isomer and can be added to the techn. BHC charged into the extraction and in small quantities to the gamma isomer concentrate charged into the recrystallization.

In order to lessen the quantity of circulating mother liquors, to regulate the specific gravity of extraction mixture and eliminate the rest of unwanted isomers of the cycle, it has been recommended to distill off the methanol from mother liquor after the second crystallization. Oily waste obtained will solidify in 72 hours. The first part of the methanol from the distillation may be used directly for the extraction mixture preparation or Lindane crystallization up to the specific gravity of 0.812 g/cm^3. The rest is to be rectified.

The crystallization temperature of gamma isomer concentrate 85% can be lowered from actual 15^{o}C to 10^{o}C as far as the content of gamma isomer is above 80%.

The modified technological process is illustrated by block diagram in Annexe 3. It represents the simplest method and way how to produce pure Lindane with minimum additional equipment. The optimization of the process parameters ought to be the objective of additional experimental work.

8.2. Machinery and equipment

The whole piping system and armature are to be replaced in preference to more convenient materials as graphite, high pressure polyethylene and polypropylene and glass, larger dimensions of diameters, insertion of gauges for visual flow control, sampling valves etc., should be considered.

The pipes must be well oriented, centered, fixed and supported. Well designed piping system is a primary condition for smooth, efficient and safe operating.

Experienced engineers and process chemists should be charged of the designing.

For the purpose of safe chlorine evaporation a boiler-feeder of hot water is to be installed, automatically regulated in dependence on the temperature in the evaporator (less than 30°C) and on the temperature of the evaporated chlorine (less than 20°C).

An emergency absorbtion and neutralization equipment for serious chlorine emissions should be installed in the store of chlorine.

The chlorination equipment ought to be situated in a separate fire protected room; the same measures have to be applied for the switchboard and switch-boxes, mainly of the light installation of chlorination reactors. Wood as construction material, e.g. for the windows and door frames is not allowed.

If the actual chlorination reactors ought to be used for further operation it is recommendable to equip the inlet tube of chlorine by fritted disks to achieve a better chlorine distribution in the reaction mixture. For a capacity of 100t/year of Lindane,3 reactors of special construction, each of 2000 l volume are needed. As best material for local conditions acid -resistant glass-lined steel is recommendable, but graphite composite materials can also be considered. To achieve a higher efficiency of chlorine absorbtion a glass or enamelled column filled with rashing rings is to be installed. To ensure a safe operation of hydrogen chloride absorbtion an automatic safty valve for the temperature limit of 30°C is to be installed.

An additional equipment for the preparation of neutralization solutions is necessary to avoid a contamination of reaction mixture by impurities, mainly by iron and rust.

In order to enable the process of neutralization a spiral film distillation apparatus is recommendable to distill off about 15-20% of benzene from the crude reaction mixture together with the main part of free chlorine and hydrogen chloride.

New condensers for each distillation apparatus ought to be installed directly above the kettles, the connecting tube being as short as possible and of a diameter about 200 mm in

order to shorten the operation time.
The less expensive granulation system consists of a vessel equipped with high speed propeller agitator, circulating feeding pump and injecting tube. The tube connecting the distillation apparatus and granulation vessel, armature and pump ought to be heated. The particle size distribution is to be within the limit from 2 mm to 4 mm in order the granules be well separable from water in a rotating sieve separator.
For the proces·· of drying, as efficient and simple equipment a vibratory fluid drier can be recommended.
Mechanization of the techn. BHC charging into the extractors would save a lot of manual work. As the space round the extractors is rather limited, the problem must be consulted with manufacturers of tiltable transport equipments.
Particularly suitable for special operation of solid unwanted isomers separation is a horizontally mounted batch filtering peeler centrifuge, which allows to achieve a content of methanol below 5% in filter cake.
In case of a modified technology 2 reactors will suffice for the extraction process and 2 extractors can be used for crystallization of intermediates. A rearrangement of inlet and outlet piping will be necessary.
Simple local aeration should be installed to the chamber filter press in oruer to shorten the operation time of discharging.
For the process of Lindane separation an additional bachwise operating pressure filter with filter basket would be recommendable. That would allow to use the actual pendulum centrifuge for the separation of intermediates.
Two additional condensers are necessary to accomplish the actual columns for the purpose of mother liquors processing. Simple outlet and charging equipment for the distillation residue disposal ought to be installed in a separate room.
In order to facilitate a crystallization regime applying lower temperatures a 20% methanol solution as brine can be used in the brine cooling station.

Local and registration thermometers should be installed into the chlorine evaporator, boiler, chlorine inlet tube, chlorination reactors, hydrogen chloride absorbtion column, distillation apparatuses, drying equipment, extractors and crystallizers, outlet of chamber filter press and centrifuge, methanol rectification column, mother liquor processing columns. Flowmeters should be installed for charging of benzene and chlorine into chlorination reactors and methanol into rectification. Manometers should be installed on the steam distributor, chlorine evaporator and distributors. Pneumatic valves should be installed on the inlet to the hydrogen chloride absorbtion column and outlet of the distribution column.

8.3. Anti-corrosive protection

The technological processes of organochlorine compounds in common are characterized by a high rate of corrosion. The decisive measures to restrict the corrosion to economically acceptable level are to be taken at the stage of designing, where the most appropriate construction materials have to be chosen. According to author's experience the glass, enamelled steel, several graphite composite materials, high pressure polyethylene and polypropylene are the most suitable materials.

For most of the tanks stainless steel is applicable.

A proper and careful handling of the equipment, mainly at the assembly, qualified preventive maintenance and scheduled external protection of the whole plant are of great importance.

Regular cleaning and painting of the machinery is inevitable. All parts of the machinery must have a two layer protection. As available primer, minium is still recommended, while the most economical surface coating is provided by chloroprene paints. The painting must be renewed every year in the frame of shutdawn for general repair, inspected regularly at least in one month periods and maintained permanently.

8.4. Analytical control

A well equipped and furnished operation laboratory is a prerequisite for successful Lindane manufacturing. Exact, systematic and well maintained records of analytical results are inevitable for a technology based mainly on experience.

Although the quality of chlorine does not vary and is guaranteed by the manufacturer, it is necessary to check at random the possible content of water in caissons of chlorine.

It is recommendable to determine the ratio of volatile matters in the technical BHC by drying the sample for 24 hours at a temperature of 40°C under an infrared lamp. The difference between the content of volatile matters and content of water equals approximately the content of monochlorobenzene and dichlorobenzene. Their higher content above 2% indicates the presence of iron ionts in the reaction mixture that catalyze the substitution chlorination and is the consequence of damaged equipment.

From the content of hydrolyzable chlorine the total content of HCH isomers is countable. Therefore the determination is important for exact feeding of technical BHC into the Lindare separation process.

It has been recommended to introduce a complete determination of all components present in technical BHC, intermediates and wastes by partition column chromatography. It enables also to compare the results obtained by gas chromatography.

Cryoscopic determination of final product's melting point is a quick and reliable method. Its introduction is a matter of importance. For this purpose the laboratory must be equipped by a Kofler's microscope as the simplest device. Thermosystem FP 800 of the firm Mettler Instrumente AG; CH-8606 Greifensee

Switzerland, which enables to evaluate graphically and numerically 3 samples paralelly at one full automatic and programmed determination, is recommendable.

The gas chromatography is necessary to provide by a complete set of standards in order to determine exactly all components present in technical BHC, intermediates and wastes.

Recovered methanol must be always tested not only by determining the water content and specific gravity but also diluting it by water. It must not show any turbidity.

A practical and simple test of iron presence in solutions circulating in BHC plant by NH_4CNS solution has been advised.

Determination of critical crystallization temperature, the most important and indispensable test for Lindane separation has been handed over at the Research Institute of Chemistry, Tirana. The test is based on dissolving a sample of gamma isomer concentrate in required quantity of methanol at the boilling point and observing the process of nucleation and crystal growth while the solution is allowed to cool slowly. As far as nucleation of gamma isomer exclusively is observed the nuclei sparkle specificly. The critical crystallization temperature at which the nucleation of alpha isomer occurs is characterized by a perceptible turbidity. The operation of crystallization and separation in the plant, if pure Lindane is to be obtained, must be carried out above the determined critical temperature and ratio of gamma isomer concentrate and methanol.

8.5. <u>Quality of the final product</u>

The standing Lindane production requires a modification of the technology including operations of gamma isomer recrystallization and unwanted isomers elimination as it is suggested in the Section 8.1.

As the successful operation of the plant depends in a high degree on the experience of the operators it is recommendable to introduce in the first period of manufacturing two qualitative categories of the final product, e.g. category A for products containing more than 99% and category B containing 95-99% of gamma isomer HCH. Such a short time measure should be consulted by the Institute of plant protection.

It is necessary for each operation of recrystallization to determine the critical crystallization temperature above which the process ought to be carried out dissolving the gamma isomer concentrate in the required quantity of methanol. The crystallizers and whole equipment have to be absolutely clean, otherwise uncontrolled nucleation occurs.

Great attention is to be paid to the separation of crystalline mass in the centrifuge where the difference of inlet suspension's and mother liquor's temperatures must be minimal. The shortest possible operation time is desirable.

Suggestions concerning analytical control are discussed in the Section 8.4.

8.6. General

Documentation of all kinds must be completed, mainly that of the technology and machinery.

Technological and analytical data have to be recorded and the records maintained on a higher level; for this purpose a more detailed system of records is necessary to elaborate.

Technological reports based on material balances have to be elaborated periodically every month.

Schedule of regular sampling and analytical control is to be elaborated.

Maintenance and repairs including electricals, instrumentals and anti-corrosive protection require a new and more efficient organization with departments and groups for special activities.

Attention must be paid to the spare parts procurements and quality control of supply.

The safety labour instructions have to be revised, amended and more elaborated. After every longer shutdown of the plant, it is recommended to inspect the equipment and especially the electricals and instrumentals commissionally, the commission being set up of the head of the plant, process chemist, electrical and mechanical engineers and specialist for safety labour and fire protection. It is strictly forbidden to preserve materials or tools of wood, cotton, paper and any organic matters easy to oxidize in the plant of BHC, as possible sources of fire in the presence of chlorine. Alarm and emergency instruction for the whole factory have to be elaborated for the case of heavy breakdown in the store of chlorine or on distribution system and consequent chlorine emission.

8.7. Research and development

For the completion of the suggested modified technological process is necessary to optimize the following parameters :

- The ratio of charged techn. BHC and extraction mixture; range 1 : 2.6 - 3.2
- The optimum crystallization temperature for gamma isomer concentrate 85%; range from 5°C to 10°C
- The optimum crystallization temperature for gamma isomer concentrate 40%; range from -5°C to 4°C
- To elaborate a regime of extraction mixture preparation
- To determine the dependance of the charged quantity of extraction mixture on the specific gravity

The obtained data ought to be verified in five subsequent cycles and a material balance elaborated according to the block diagram, Annexe 3.

From view-point of further technical development and decision making process two measures are of great importance :

- To invite quotations and offers for a turnkey plant construction from producer's of repute and especially for chlorination reactors; granulation and drying equipment; the invitation letters should be formulated in a very thorough way in order to receive the most detailed information

- In case that other alternative should be preferred an engineering study ought to be elaborated

According to the Backstopping Officer's instructions a joint summary of two UNIDO consultants reports, conclusions and recommendations has been elaborated, see Chapter 11.
As it has been based mainly on author's findings and conclusions resulting of the compex analysis, they have been left out of this Section in order to avoid duplicity.

9. ESTIMATION OF INVESTMENT COSTS

Considering in thorough way the actual critical state of the process machinery of both BHC and Lindane plants, the fact that greater part of the equipment does not suit perfectly to its purpose and there is no real know-how of the process, the author has arrived at the conclusion that a turnkey plant purchase would be the most reliable way to construct a new Lindane manufacturing capacity. For this purpose quotations and offers of the foremost manufacturers have to be invited, evaluated and selected.
Anyway, there is a less expensive alternative,to purchase the know-how, machinery & equipment and basic engineering, and to provide the detail engineering, civil work, assembly and other activities connected with the construction process by inland organizations. Estimation of construction costs of this alternative is the objective of the following section.

9.1. Construction costs of a new plant

Utilities at battery limit are supposed. Plant area, process building and structure with all auxiliary objects of the system with some additional civil works are expected to be used. Brine cooling station being in a good state is expected to be used and is not calculated in investment costs. Minimum level of instrumental is provided with no remote control. Stores for solid wastes are not included.

Detail engineering, equipment purchase and erection is supposed to be carried out by Albanian organizations.

For the complete absence of quotations and price data as well as short term, the estimation can be considered only as a rough technical assessment.

As the most expensive items of the machinery and equipment have a higher output as it corresponds to the production of

100 t/year of the final product, the estimation has been elaborated for a more economical plant capacity of 150 t/year of Lindane.

Engineering	245 000 USD
Process machinery and equipment	
- BHC plant	1 283 000 USD
- Lindane plant	1 519 000 USD
Assembly	475 000 USD
Steel construction and decks	184 000 USD
Piping and armature	392 000 USD
Insulation	42 000 USD
Painting	26 000 USD
Scaffolding	22 000 USD
Aeration	67 000 USD
Instrumental	223 000 USD
Electrical	252 000 USD
Civil works	304 000 USD
Site costs	74 000 USD
Reserve	580 000 USD
Total	5 688 000 USD

Investor's activities and engineering, spare parts of inland production and start up costs are not included.

9.2. Plant rehabilitation costs

Although the autor has not recommended a rehabilitation of BHC and Lindane plants, being aware of all risks involved, costs estimation has been elaborated in order to illustrate the investment requirements.

The major factors increasing the amount of risks are mainly as follows :

- The whole machinery is corroded to a certain extent and its service life is limited.

- Great part of the equipment does not suit properly to its purpose.
- The process building, structure and stages as far as the machinery is not completely dismounted do not allow a general rearrangement of the equipment and piping system as necessity demands.
- The actual technology does not give a guarantee of reproducible qualitative parameters of the final product and of standing economical manufacturing.

As a result, in some aspects a lower technical level is predisposed to the whole concept of the rehabilitation.

An attempt has been made to elaborate the estimation of the rehabilitation costs for an intensified capacity of 150t/year of Lindane in order to illustrate the difference between construction costs of a new plant, Section 9.1, and rehabilitation costs in a more comparable way. The fact, that for a rehabilitation is not possible to count on a complete dismounting of the machinery to arrange the new equipment in the most purposeful way and the fact that the most valuable and expensive items of the machinery ought to be used, do not allow to achieve higher capacity in a reasonable way than 100 t/year of Lindane, for which the following estimation has been elaborated.

Engineering	263 000 USD
Process machinery and equipment	
- BHC plant	1012 000 USD
- Lindane plant	492 000 USD
Assembly	364 000 USD
Steel construction and decks	122 000 USD
Piping and armature	249 000 USD
Insulation	34 000 USD
Painting	24 000 USD
Scaffolding	19 000 USD
Aeration	36 000 USD

Instrumental		141 000 USD
Electrical		159 000 USD
Civil works		220 000 USD
Site costs		66 000 USD
Reserve		350 000 USD
	Total	3 551 000 USD

Investor's activities and engineering, spare parts of inland production and start up costs are not included.

10. SUMMARY

During his mission in Albania, Durres, from 1st June, 1989 to 26th June, 1989 the author has inspected the overall conditions of the plant, reviewed the machinery and equipment and observed the technological process, although not at full operation. Assessment of the technology, based on the study of available technical documentation, records of analytical and operation control, personal observations and findings has been elaborated in the form of complex analysis. Any occasion has been used to hand over experience and knowledge of the process and consult the problems at everyday routine visits of the factory and institute.

Recommendations and conclusions reffered to in Chapter 8 and 11 have been discussed in general at the Committee of Science and Technology, Research Institute of Chemistry and Management of Chemical Works, Durres.

As two UNIDO Experts have assisted the project authorities in the rehabilitation of Lindane manufacturing plant at Durres, Albania, one for technology assessment and the other for anticorrosive protection, a brief joint report has been elaborated into which the most important common conclusions and recommendations are included

11. JOINT SUMMARY OF UNIDO CONSULTANTS REPORTS

Main observations, conclusive remarks and recommendations offred jointly by the two UNIDO experts;

1.0 Introduction :

Our following observations and overall conclusions are based on a complex analysis of process, all the equipment and the present state of affairs that exist in reality at the Lindane plant. These are based on a limited and partial study and review of the entire operational and maintenance aspects of BHC and Lindane plant, as also the plants were not in full operation throughout our stay there. Our work was further limited due to several constraints such as absence of required documentations, operational and analytical records, history of plant operation and other necessary technical informations.

2.0. Overall conclusions on the present state of affairs :

2.1. The original technological process was supposed to be on the process licence from the Chinese People's Republic. However, as the technical cooperation between the two countries subsequently got interrupted and also as there was no formal contract signed between the two countries, the technology and the further detailed engineering was accomplished within the country mainly by the Institute of Chemistry, Tirana. With the result, the technological process as well as the process equipment was simplified, which do not really match with the requirements of original technology intended by the lincesor. The present technology and the equipment and machinery do not allow to produce final product with quality parameters to the requirements of pure Lindane (99.0% - WHO), and to the required capacity.

2.2. Under the circumstances, where all the main enamelled reactors were supplied by the lincesor, some valuable process equipment were, however, procured by the user/ local plant management. Also, in the author's opinion, the enamelled reactors and the armature, so supplied, are not of guaranteed first class quality.

2.3. The overall situation at the Lindane plant, both from operational and maintenance aspects, is highly unsatisfactory and is a matter of great concern, as there is not going to be a simple and straight solution to this complex problem.

2.4. In our opinion, the overall state of health of majority of the equipment, pipings and fittings etc. are very poor due to the high level of internal and external corrosion, lack of operational and maintenance skills and absence of systematic preventive maintenance of mechanical, electrical and process instrumentations.

2.5. Even though the process and the service conditions in the Lindane plant is highly corrosive, corrosion can certainly be considerably reduced by using the right construction materials, adopting good inspection and maintenance practices, by formulating and following a well-knit programme of equipment condition monitoring and corrosion control.

2.6. Due to the exacting technology and machinery requirements, it is an absolute necessity to achieve a state of basically higher work organisation and efficiency in all fields of activities like operation, maintenance, analytical and corrosion control.

2.7. It would appear from the facts stated above that, in reality, the know-how presently available with them is not adequate to achieve the desired yield of pure Lindane at the required capacity and is also not a sufficient base neither for basic and detailed engineering nor for rehabilitation.

3.0. <u>Recommendations</u> :

In its present state of affair at Linadane plant as described above, and appreciating the above conclusions that under the circumstances, rehabilitation of Lindane plant, so as to fulfill all the requirements of a modern, efficient and an economically working plant, will not be possible, we suggest the following alternatives;

3.1. It is recommended to go for a new Lindane plant on a turnkey basis by inviting quotations and offers for know-how of the process, machinery, equipment and construction from reputed Lindane manufacturers and equipment suppliers.

3.2. A less expensive alternative would be to borrow process know-how, machinery, equipment and basic engineering from other countries, but with indegeneous detailed engineering and construction including assembly. This will, nevertheless, have certain amount of risk mainly at the stages of detailed engineering and construction. This alternative should, therefore, be considered carefully keeping in view the indegeneous capability and the indicated risk and the decision must be left completely to the Albanian authorities.

3.3. Though it is not our recommendation, some modifications, partial replacements and inclusions of some additional equipment can be considered. It should, however, be made clear that this will not be a full-proof proposal and will not guarantee an exclusive production of pure Lindane but a concentrate of high gamma isomer content will be produced to a certain extent as well.

This will also call for a thorough investigation on the indegeneous capability concerning additional research, engineering, machinery procurement and the organising competency required for construction.

In any way, quotations and offers for most important items of machinery and equipment would be necessary such as a system of chlorination reactors, granulation and drying equipment, separation equipment and several others. It can thus be seen that this alternative will also, by no means, be an inexpensive proposition.

3.4. During the period of preparation and the construction of a new Lindane plant, the following activities/consultancy services can be assisted by UNIDO consultants, by a mutual agreement between UNIDO and Government of Albania.

3.4.1. Formulations of enquiries for inviting quotations and offers for a turnkey plant or for individual machinery and equipment.

3.4.2. Evaluation and selection of recommendable quotations and offers.

3.4.3. Assistance at the basic engineering, auditing and design review of the basic and detailed engineering.

3.4.4. Monitoring and consultancy at the decisive stages of construction on site.

3.4.5. Plant construction commissioning assistance.

3.4.6. Scholling and training of the plant staff of all disciplines in several areas of importance.

3.4.7. Technical assistence during the plant start-up period.

3.4.8. Evaluation of plant performance at the end of one year operation and offer suitable suggestion for improvements.

3.4.9. Periodical reviews of operational and maintenance activities and offer suggestions for their optimisation.

4.0 General indication :

4.1. The present wordwide situation of Lindane, from the point of view of its application, is rather uncertain. Even though Lindane is a valuable insecticide, manufacturing at the large scale would create toxic side products, unwanted isomers, which in the long run could cause problems of storage and disposal. So any new technology should take into account conversion of side products to usable chemical intermediates.

4.2. Albanian Government should also take into account another alternative of investing money for the production of safer and more valuable pesticides useful to Albania, rather than spending money on one product dedicated plant for the production of Lindane. The recent trend is to go for multipurpose pesticide plants using batch processes rather than one product dedicated plants.(see annex 4 - for possible options).

28 June, 1989, UNIDO Headquarters, Vienna.

12. GLOSSARY OF TERMS AND SYMBOLS

Critical Crystallization Temperature - The lowest temperature characteristic for every batch at which a crystallization of Lindane can be successfully carried out

Crude Reaction Mixture - Solution obtained by the process of benzene chlorination

EM, Extraction Mixture - Solution for extraction of techn. BHC prepared by mixing methanol, recovered methanol and mother liquors

GIC 85 - Gamma isomer concentrate containing approximately 85% of gamma isomer of HCH

GIC 40 - Gamma isomer concentrate containing approximately 40% of gamma isomer of HCH

HCH - Hexachlorocyclohexane

Lindane - Common name for technical product containing at least 99% of gamma isomer of 1, 2, 3, 4, 5, 6 hexachlorocyclohexane as active substance (AFNOR-ISO)

LW - Liquid waste from alcaline absorbtion of hydrogen chloride

ML 85; 40 - Mother liquor from the separation process of gamma isomer concentrate 85; 40%

ML 99 - Mother liquor from the separation process of Lindane

Techn. BHC - Technical benzenehexachloride, a mixture of isomers of hexachlorocyclohexane and by-products of the additional chlorination of benzene; raw material for gamma isomer of HCH separation

W 1, Waste 1 - Solid waste containing mainly alpha and beta isomers of HCH and less than 1.5%

of gamma isomer of HCH

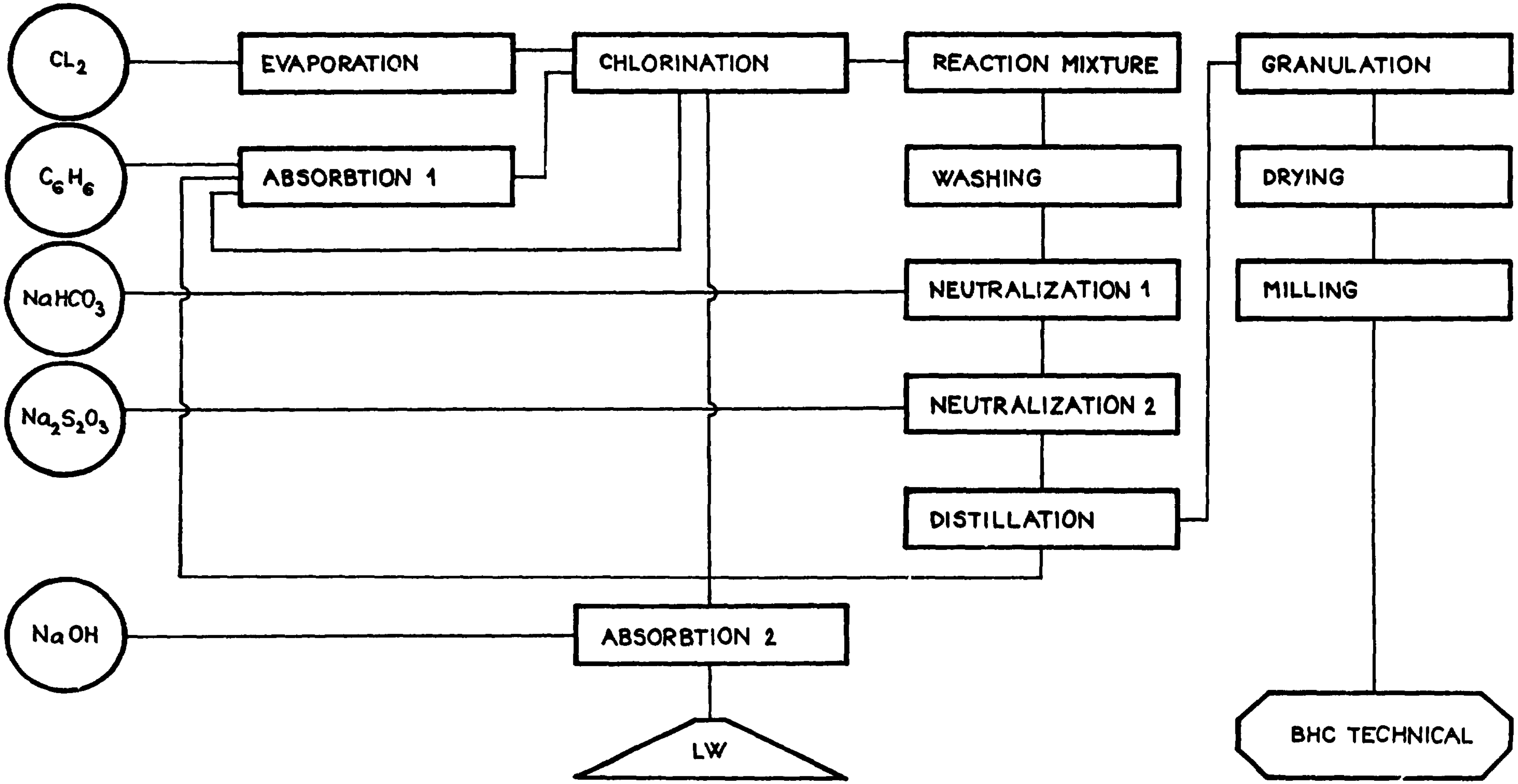
W 2, Waste 2 - Solid waste containing alpha, delta and epsilon isomer of HCH, hepta and octa-chlorocyclohexane and less than 18% of gamma isomer of HCH

13. ACKNOWLEDGEMENT

It is the author's earnest wish to express his sincere gratitude to all who cooperated during his activity in Albania and his high appreciation of the whole-hearted welcome and hospitality proved at several occasions.

14. ANNEXES

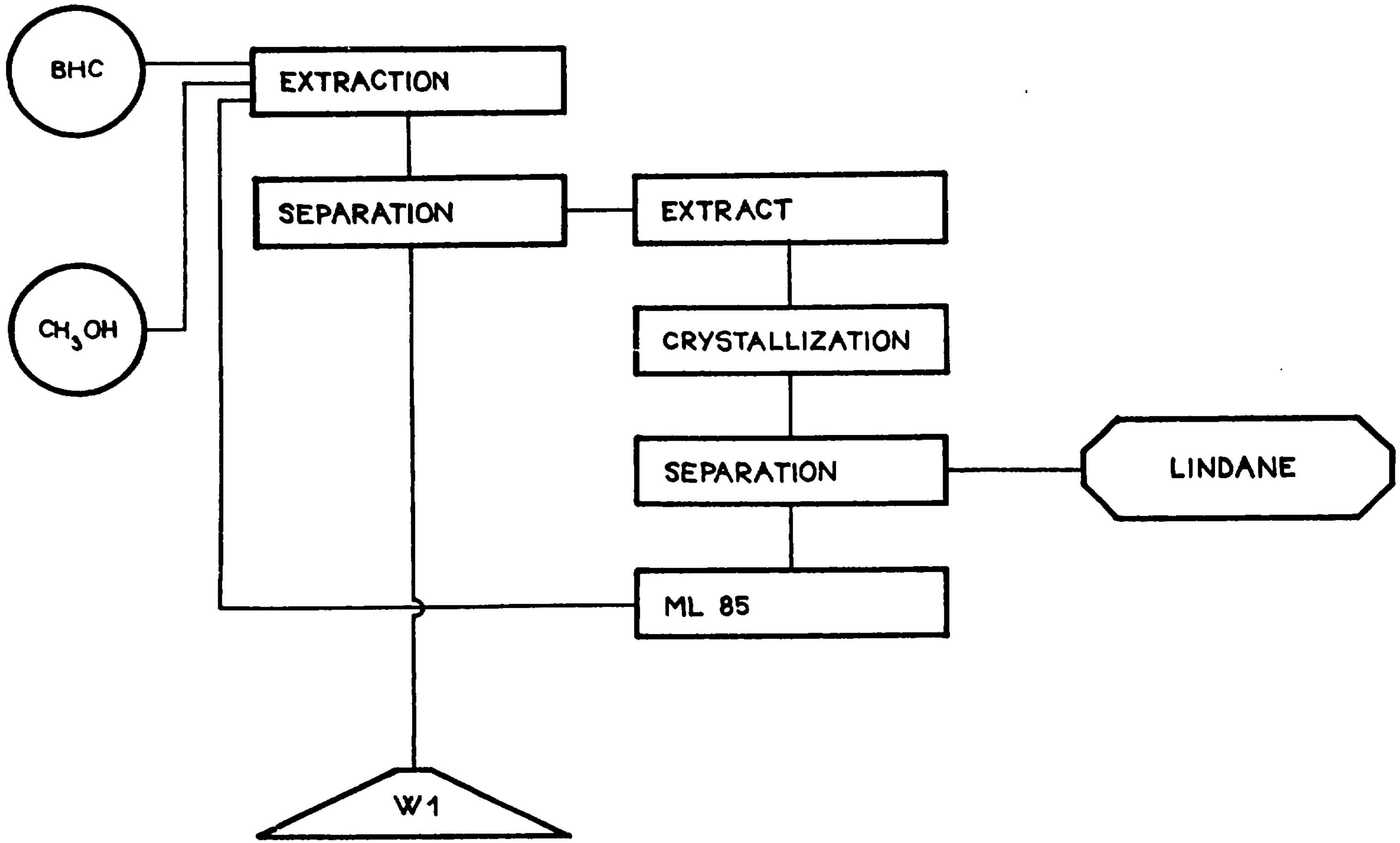
BHC PLANT BLOCK DIAGRAM



ANNEXE 1

LINDANE SEPARATION PLANT BLOCK DIAGRAM

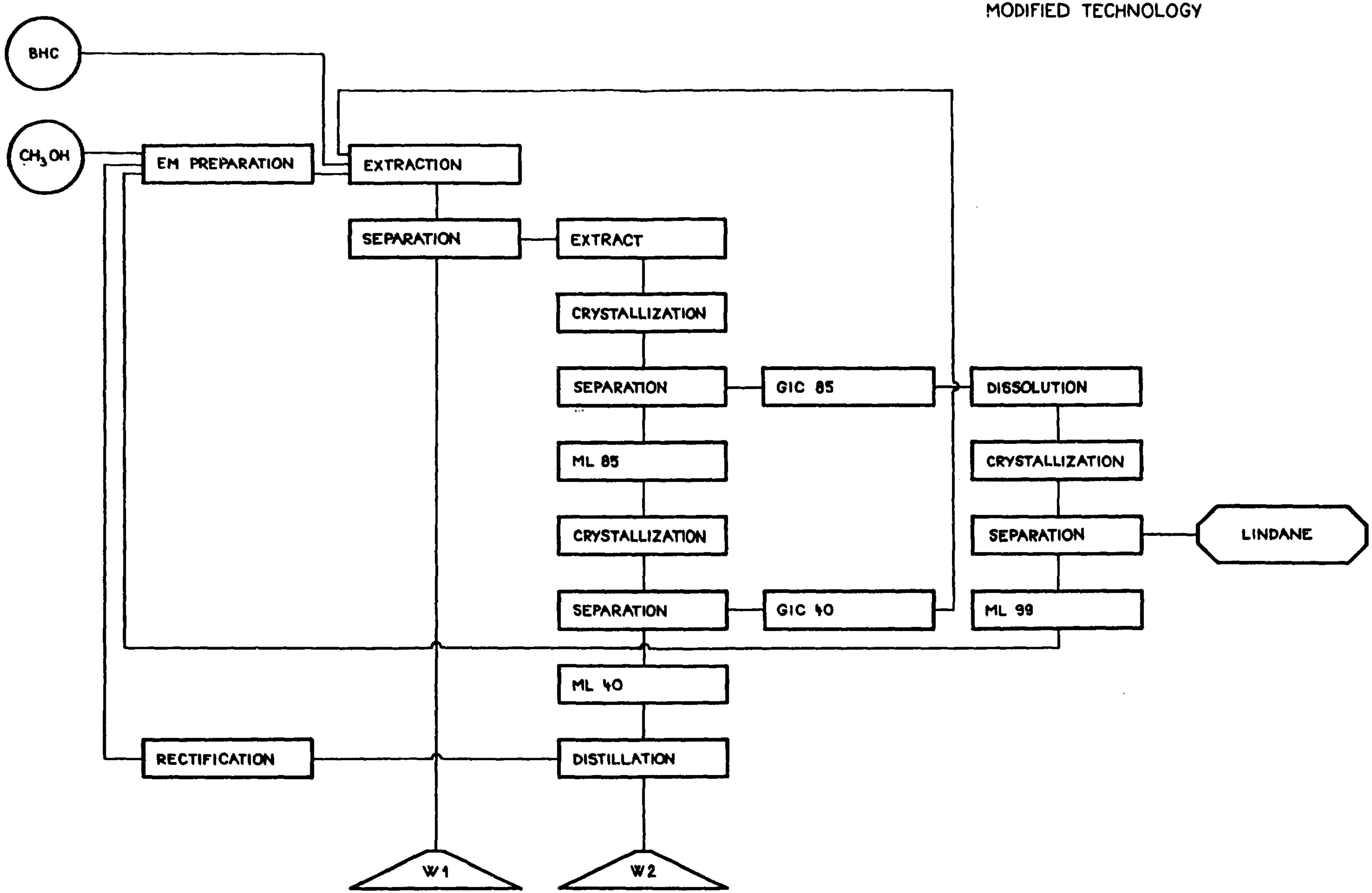
FACTUAL STATE



ANNEXE 2

LINDANE SEPARATION PLANT BLOCK DIAGRAM

MODIFIED TECHNOLOGY



ANNEXE 4

INTRODUCTION

In connection with the intention of the Government of Albanian People's Republic to construct a new capacity of pesticidal products, several know-how available in the Czechoslovak Socialist Republic can be taken into consideration. Following data represent a basic technical information about the products and technologies most recommendable.

1. TRADE MARK : **METATION E-50**

Formulation : Emulsifiable concentrate

Content of active ingredient : 50 % w

Active ingredient

- Common name : Fenitrothion
- Chemical name : O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate
- Chemical structure : see Annexe 5
- Molecular formula : $C_9H_{12}NO_5PS$
- Molecular mass : 277,2

Qualitative parameters :

- Content of active ingredient : 50 ± 2,5 % w
- Purity of active ingredient : min. 94 % w
- Content of water : max. 0,5 % w
- Acidity : max. 0.3 % w
- Emulsion stability; 20°C; 2 hours : max. 3 ml of cream, no oil separation

Uses : It is a potent contact insecticide, effective against a wide range of penetrating, chewing and sucking insect pests (e.g. coffee leafminers, locusts, rice stem borers, wheat bugs) on field crops, vegetable crops, orchards and ornamental gardens. It is also effective against household and nuisance insects. Its effectiveness as a vector control agent for malaria is confermed by WHO.

Toxicology : Relatively low mammalian toxicity is characterized by acute oral LD_{50} for rats 1500 mg/kg.

Alternative products : Sumithion, fa Sumitomo Chem., Co., Japan
Folithion, fa Bayer, A.G., FRG

Main technological stages :

- Synthesis of O,O-dimethylchlorophosphorothioate
- Synthesis of sodium 3-methyl-4-nitrophenolate
- Condensation of intermediates
- Formulation

Batchwise operation, limited scope of remote control.

Recommended production capacity : 2000 t/y of Metation E-50, or
1000 t/y of fenitrothion

Annual operation hours : 7200;
four shift non-stor eration

Manpower requirements :

- Personnel	4
- Formen	4
- Operaters	59
Total	67

Specific consumption figures :

-Raw materials	
Phosphorus chlorite	0,600 t/t
Sulphur	0,140 t/t
Methanol	0,700 t/t
M-cresol	0,360 t/t
Sulphuric acid	2,200 t/t
Sodium hydroxide	0,430 t/t
Xylene	0,340 t/t
-Utilities	
Electric power	780 kWh/t
Steam	42 GJ/t
Water	200 m^3/t

General : The technological process is simple and reliable. The lower purity of active ingredient compared to the FAO standard (difference of 2 % w) is compensated by low production costs, while the full-value biological activity is preserved. The process machinery and equipment allow also to produce other organophosphorous insecticides as ethyl-parathion and methyl-parathion.

2. TRADE MARK : ZEAZIN 50 DP

Formulation : Wettable powder

Content of active ingredient : 50 % w

Active ingredient

- Common name : Atrazine
- Chemical name : 2-chloro-4-ethylamino-6-isopropyl-amino-1,3,5-triazine
- Chemical structure : see Annexe 5
- Molecular formula : $C_8H_{14}N_5Cl$
- Molecular mass : 215,66

Qualitative parameters

- Content of active ingredient : 50 $\pm$ 2,5 % w
- Purity of active ingredient : min. 92 % w
- Suspension stability : min. 80 % w
- Wettability : max. 45 sec.

Uses : Zeazin 50 WP is a selective pre- and postemergent herbicide used in asparagus, forestry, grasslands, grass crops, maize, pineapple, roses, sorghum, sugarcane and non-crop areas; in plantations of apples, pears and wineyards.

Toxicology : Acute oral LD_{50} for rats 3600-6000 mg/kg.

Alternative products :

GESAPRIM 50 WP; GESAPRIM 80 WP, fa Ciba-Geigy

ATRADEX 50 WP, fa ICI

FOGARD WP, fa Siapa

...

Main technological stages :

- Condensation of cyanurchloride and isopropylamine
- Condensation of 2,6-dichloro-4-isopropylamino-1,3,5-triazine and ethylamine
- Distillation of the solvent
- Separation of the technical atrazine
- Drying and milling of the technical atrazine
- Formulation

Batchwise operation, limited scope of remote control.

Recommended production capacity : 3000 t/y of Zeazin 50 DP,or
1500 t/y of Atrazine

Annual operation hours : 7200;
four shift non-stop operation

Manpower requirements :

- Personnel	4
- Formen	4
- Operators	32
Total	40

Specific consumption figures :

- Raw materials	
Cyanochloride	0,480 t/t
Chlorobenzene	0,053 t/t
Isopropylamine	0,163 t/t
Ethylamine	0,125 t/t
Sodium hydroxide	0,232 t/t
Formulation components	0,527 t/t
-Utilities	
Electric power	261 kWh/t
Steam	26,4 GJ/t
Water	400,0 m^3/t

General : The technological process is simple, reliable and economical, which compensate the lower purity of active ingredient compared to the FAO standard (difference of 3 % w).

The process machinery and equipement represents a multi-purpose plant that allows to produce :

- Cyanazine
  2-chloro-4-(1-cyano-1-methyethylamino)-6-ethylamino-1,3,5-triazine
- Propazine
  2-chloro-4,6-bis (isopropylamino)-1,3,5-triazine
- Simazine
  2-chloro-4,6-bis (ethylamino)-5-triazine
- Prometryn
  2,4-bis(isopropylamino)-6-methylthio-1,3,5-triazine
- Terbutryn
  2-tert-butylamino-4-ethylamino-6-methylthio-1,3,5-triazine

The basic raw material for cyanazine, propazine and simazine is cyanurchloride, while the synthesis of terbutryn and prometryn is based on methylthiodichlorotriazine.

3. TRADE MARK : **AMINEX PUR**

Formulation : Soluble concentrate

Content of active ingredient : 28 % w

Active ingredient

- Common name : MCPA
- Chemical name : (4-chloro-2-methylphenoxy)-acetic acid
- Chemical structure : see Annexe 5
- Molecular formula : $C_9H_9ClO_3$
- Molecular mass : 200,6

Qualitative parameters

- Content of active ingredient : 28,0 ± 1,4 % w
- Purity of active ingredient : 83 % w
- Content of chlorinated cresols : max.1 % w
- Content of free dimethylamonium : max. 0,2 % w
- Specific gravity : 1.140 kg/m^3

Uses : It is a systemic hormone-type selective herbicide, readily absorbed by leaves and roots. Its uses include the control of annual and perennial weeds in cereals, grassland and turf.

Toxicology : Acute oral LD_{50} for rats 2100 mg/kg.

Alternative products : Agroxone, fa ICI Plant Protection Div.
Agritox, fa May and Baker, Ltd.
Phenoxylene Plus, fa FBC Limited

Main technological stages :

- Neutralization of monochloroacetic acid
- Neutralization of o-cresol
- Condensation of sodium cresolate and sodium chloroacetate
- Chlorination of the natium salt of monochloroacetic acid
- Separation of MCPA
- Neutralization and formulation

Batchwise operation, limited scope of remote control.

Recommended production capacity : 6000 t/y of Aminex Pur

Annual operation hours : 7200;
four shift non-stop operation

Manpower requirements :

- Personnel 4
- Formen 4

- Operators	29
Total	37

Specific consumption figures :

- Row materials

O-cresol	0,226 t/t
Monochloroacetic acid	0,229 t/t
Caustic soda	0,153 t/t
Sodium hypochlorite	2,000 t/t
Hydrochloric acid (as 100 % w)	0,210 t/t
Dimethylamonium (as 100 % w)	0,076 t/t
Natrium hydroxide (as 100 % w)	0,200 t/t

- Utilities

Electric power	211.0 kWh/t
Steam	100,0 GJ/t
Water	12,5 m^3/t

General : The lower purity of active ingredient is compensated by exraordinary low production costs, reliability and simplicity of the technology.
Several mixtures with active ingredients as flurenol. dicamba, benazolin, 2,4-DB. 2,4-D, ioxynil and others can be prepared by the equipment of the plant.

4. TRADE MARK NOVOZIR Mn - 80

Formulation : Wettable powder

Content of active ingredient : 80 % w

Active ingredient

- Common name : Mancozeb
- Chemical name : Manganese ethylenebisdithiocarbamate polymeric complex with zinc salt
- Chemical structure : see Annexe 5

- Molecular formula : $(C_6H_6N_2S_4Mn)_x (Zn)_y$
- Molecular mass : 271,0

Qualitative parameters

- Content of active ingredients	:	80 ± 2,5 % w
- Purity of active ingredient	:	min. 85 % w
- Content of Mn in a.i.	:	min. 20 % w
- Content of Zn in a.i.	:	min. 2,5 % w
- Content of water	:	max. 2,0 % w
- Content of ethylenethiourea	:	max. 0,2 % w
- Suspension stability	:	min. 60 % w
- Wettability	:	max. 45 sec.

Uses : It is a protective fungicide effective against a wide range of foliage fungal diseases used to protect field crops, vegetable, fruit and ornamentals.

Toxicology : Preparation is of low mammalian toxicity; acute oral LD_{50} for rats 8000 mg/kg.

Alternative products : Dithane, fa Rohm and Haas, Co.. USA
Manzate, fa Du Pont and Co.. Inc., USA
Nemispor, fa Montedison, S.p.A, Italy

Main technological stages :

- Synthesis of ethylenebisdithiocarbamate complex
- Separation and drying of the a.i.
- Formulation

Batchwise operation; remote control of main operations.

Specific consumption figures :

- Row materials

Carbon disulphide (100 %)	0,600 t/t
Ethylenediamine (100 %)	0,215 t/t
Manganous sulphate (100 %)	0,560 t/t
Zinc sulphate (100 %)	0,072 t/t

- Utilities

Electric power	1500 kWh/t
Steam	59 GJ/t
Water	270 m^3/t

Recommended production capacity : 1500 t/y of Novozir Mn - 80

Annual operation hours : 7200;
four shift non-stop operation

Manpower requirements :

- Personnel	4
- Formen	4
- Operators	38
Total	46

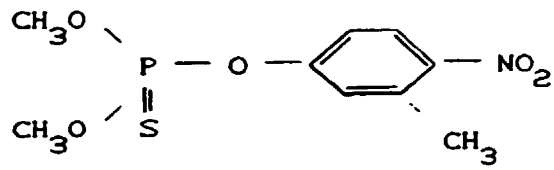
General : The product is stable under normal storage conditions but decomposed at high temperatures by moisture and by acid.

Purity of active ingredient corresponds to the standard of FAO.

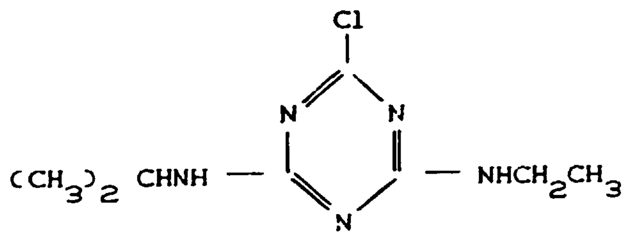
The process machinary and equipment can also be used for the purpose of manufacturing zineb, ziram, maneb or some other complexes of ethylenebisdithiocarbamate.

ANNEXE 5

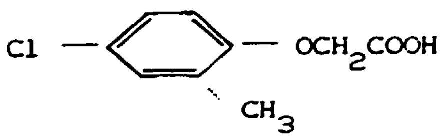
Fenitrothion :



Atrazine :



MCPA :



Mancozeb :

$[-SCS.NHCH_2CH_2NHCS.S.Mn-]_x\ (Zn)_y$