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RESTRICTED

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#### ASSISTANCE FOR ZINEB AND MANEB

PRODUCTION,

DP/TUR/76/061,

TURKEY .

#### Terminal report

Prepared for the Government of Turkey -8 JUN 1978 by the United Mations Industrial Development Organization, executing agency for the United Mations Development Programme

#### Based on the work of Cesare A. Peri, chemist

United Mations Industrial Development Organisation

Vienna

id.78-348

#### Explanatory notes

References to dollars (\$) are to United States dollars, unless otherwise stated.

The monetary unit in Turkey is the Turkish lira (LT). During the period covered by the report, the value of the LT in relation to the United States dollar was SUS 1 = LT 19.25.

The following abbreviations are used in this report:

TZDK Türkiye Zirai Donatim Kurumu (General Directorate of Agricultural Supplies) .

The following technical abbreviations are used in this report:

NH\_DTC ammonium ethylenbisdithiocarbamate

DTC dithiocarbamates

- EDA ethylenediamine
- h hour
- 1 litre
- t metric ton
- ang manager

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#### ABSTRACT

A feasibility study on the project "Assistance for sineb and maneb production" (DP/TUR/76/061) has been carried out in a two-months mission starting from 23 November 1977. The main results of the study are as follows:

1. The foreseen consumption of dithiocarbamates fungicides in Turkey amounts to about 2,125 t in 1980 and 3,200 t in 1984.

2. Turkish agriculture will need mancozeb besides zineb and maneb.

3. A feasibility study on such a type of industrial plant has been carried out, and this report gives details on raw-materials, chemistry, procedure, yields, management, equipment.

4. The total investment cost has been estimated at about LT 90 million: a part of the equipment (about 26) has to be imported.

5. The investment profitability against the international selling prices has been calculated: only sineb production causes loss of money, while an attractive profitability rises from maneb and mancozeb production. Anyway, the overall return on investment is 10% in 1980 and 25% in 1984.

6. Foreign exchange savings amount to \$12 million for the 1980-1984 period.

7. Plant location has been envisaged in the north-west area of Turkey, in Orhangasi (Isnik lake).



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#### INTRODUCTION

The increased consumption of fungicides in Turkey led the Turkish Government to request UNDP aid for establishing a local production of DTC derivatives. The initial request of the Turkish Government was for a zineb and maneb production but after this request they wanted to consider the manufacturing of mancozeb too.

Owing to the technical possibility of producing the three fungicides in the same plant, this feasibility study will consider this additional request, according to the agreement of UNIDO.

The requirement of these fungicides is very important for the country, since they are widely used in the protection of tobacco, an important export cash crop, against <u>peronospora</u> tabacina, and vineyards and orchards.

Current annual imports in these products amount to more than \$500,000 (\$680,000 in 1975 and \$580,000 in 1976), so their production has been included in the third Five-Year Development Programme in the "Future Ingredient Production Facilities" section of the recommendations of the Agricultural Sub-Committee.

No work was carried out by UNIDO in the same field previously in Turkey.

The Turkish Government has decided to examine the possibility of a local manufacturing of DTC fungicides, consequently on 21 December 1976 requested expert assistance from UNDP in carrying out a feasibility study of zineb and maneb production in Turkey.

In response to this request UNDP approved the request on 21 April 1977 and set up a project DP/TUR/76/061/B/01/37 entitled "Assistance for zineb and maneb production", with UNIDO as the executing agency and TZDK of the Ministry of Agricultural, Government of Turkey, as the Government counterpart.

Therefore, Mr. C.A. Peri, UNIDO consultant, undertook a two months mission, beginning from 23 November 1977, to assist TZDK in the feasibility study of such a production. The whole study would have been carried out by two UNIDO experts (Mr. Peri and Mr. Sartori) but Mr. Sartori, expert in tender specifications, did not accept the job. So, this study does not deal with this last item. During the various meetings with TZDK managers, they agreed to first carry out the feasibility study and to get the tender specifications after the examination of the feasibility study.

The objective of the project was to examine the feasibility of establishing a plant for DTC manufacturing in Turkey.

#### I. THE MARKET

# The demand and the offer of the last five years

Zineb, maneb and mancozeb are imported in Turkey, both as finished products and as technical active ingredients. In this second case they are formulated by local companies. In comparison to previous years, importation of these DTC fungicides has increased in the last five years. Table 1 shows the total amount of imported zineb, maneb and mancozeb.

Year	Zineb	Maneb	Mancozeb
1972	416.8	144.4	1 <b>6.</b> 6
1973	5 <b>26.4</b>	-	-
1974	170.5	35.9	36.0
1975	460.1	56 <b>.0</b>	60 <b>.</b> 0
1976	604.1	40.0	36.0

Table 1. DTC imported in Turkey in the last five years (Tons of active ingredient)

According to the programmes stated by the Turkish Agricultural Protection Agency (Zirai Mücadele ve Karantina Genel Müdürlügü) the calculated requirements for the last five years should have been as shown in table 2.

Year	Zineb	Maneb	Manco zeb
1973	284.0	211.2	371.6
1974	25 <b>6.0</b>	94.5	673.6
1975	455 <b>•9</b>	223.2	531.4
1976	373.0	263.4	910.4
1977	55 <b>7.0</b>	271.2	1145.6

Table 2. DTC needed according to the agricultural protection programme (Tons of active ingredient)

a/ Mancozeb figures are based on the hypothesis that this fungicide should have been used as a substitute for mercury seed dressing chemicals.

#### Capacity of the DTC plant

The capacity of the DTC plant has been established by TZDK on the following basis:

......

Mercury seed dressing chemicals will be prohibited in the near future, according to international rules

In the case of a local DTC production the current usage of 55-60% for the main applications, i.e. spraying tobacco, vineyards and orchardr, will be increased up to 100%

Turkish Government is ready to take all measures so that zineb, maneb and maneogeb local production will be used instead of imported fungicides

Especially manaples will be encouraged because of its synergist activity in combined application with other fungicides

Zineb, maneb and mancheb will be used against the following pathogen fungi and bacteria on fruits, vegetables, industrial crops and cereals: <u>Venturia</u>, <u>Gymnosporangium</u>, <u>Monilia</u>, <u>Glasterosporium</u>, <u>Alternaria</u>, <u>Uromyces</u>, <u>Peronospora</u>, <u>Bremia</u>, <u>Phytohthora</u>, <u>Botrytis</u>, <u>Septaria</u>, <u>Cercospora</u>, <u>Plasmopora</u>, <u>Xanthomanus</u> <u>Tillatia</u>, <u>Ustilago</u>.

Taking into account all these considerations, TZDK has established the following requirements and plant captor base:

Year	Zineb	Maneb	Mancozeb	Total	Percentage coverage of crops
1980	525	300	1 300	2 <b>125</b>	65
<b>19</b> 81	600	350	1 500	2 <b>4</b> 50	75
<b>19</b> 82	675	375	1 700	2 750	35
<b>19</b> 83	725	400	1 800	2 <b>9</b> 25	90
<b>19</b> 84	8 <b>00</b>	450	2 <b>000</b>	3 <b>2</b> 50	100

Table 3. Capacity of the DTC plant (Tons of active ingredients)

#### II. GENERAL SCHEME OF THE MANUFACTURING OF ZINEB, MANEB AND MANCOZEB

#### Zineb

Zineb is the sinc salt of the etylene-bisdithiocarbanic acid.

#### Main reactions

By reaction among CS<sub>2</sub>, EDA and a stronger base.

The reactions occur through two main steps:

$$s \stackrel{\text{CH}_2}{\underset{\text{CH}_2}{\text{CH}_2}{\text{-}}} \stackrel{\text{NH}_2}{\underset{\text{NH}_2}{\text{+}}} \stackrel{\text{CS}_2}{\underset{\text{C}}{\text{+}}} \stackrel{\text{NH}_3}{\underset{\text{CH}_2}{\text{-}}} \stackrel{\text{NH}}{\underset{\text{CH}_2}{\text{-}}} \stackrel{\text{NH}}{\underset{\text{CH}_2}{\text{-}}} \stackrel{\text{CH}_2}{\underset{\text{CH}_2}{\text{-}}} \stackrel{\text{NH}}} \stackrel{\text{CH}_2}{\underset{\text{CH}_2}{\text{-}} \stackrel{\text{NH}}} \stackrel{\text{CH}_2}{\underset{\text{CH}_2}{\text{-}}} \stackrel{\text{NH}}}{\underset{\text{CH}_2}{\underset{\text{CH}_2}{\text{-}}} \stackrel{\text{NH}}} \stackrel{\text{CH}_2}{\underset{\text{CH}_2}{\underset{\text{CH}_2}{\text{-}}} \stackrel{\text{NH}}} \stackrel{\text{CH}_2}{\underset{\text{CH}_2}{\underset{\text{CH}_2}{\text{-}}} \stackrel{\text{NH}}} \stackrel{\text{CH}_2}{\underset{\text{CH}_2}{\underset{\text{CH}_2}{\underset{\text{CH}_2}{\underset{\text{CH}_2}{\text{-}}} \stackrel{\text{NH}}} \stackrel{\text{CH}_2}{\underset{\text{C$$

The global reaction is as follows:

$$\begin{array}{c} CH_2 - NH_2 \\ (H_2 - NH_2 + 2CS_2 + 2NH_3 \\ CH_2 - NH_2 \end{array} \xrightarrow{\begin{subarray}{c} CH_2 - NH - C - SNH_4 \\ (H_2 - NH - C - SNH_4 + 22.1 \ koal/m \\ CH_2 - NH - C - SNH_4 \end{array}$$

a

Precipitation of sineb

The reaction of the  $\mathbb{NH}_4$  DTC and a sinc salt provides the product and annonium sulphate as by-product:



- 10 -

#### Side reactions

Under some conditions the following other reactions might occur:

- 11 -

Reaction between CS2 and NH3 with the formation of ammonium dithiocarbamate:

 $\text{CS}_2 + 2\text{NH}_3 - - \rightarrow \text{NH}_2 - \text{C}_{H} - \text{SNH}_4$ 

This reaction occurs when a large excess of ammonia or insufficient EDA are present.

Decomposition of the aforesaid ammonium dithiocarbamate:

$$2\mathrm{NH}_2 - \mathrm{G} - \mathrm{SNH}_4 - - \rightarrow (\mathrm{NH}_4)_2 \mathrm{S} + \mathrm{NH}_4 \mathrm{SCN} + \mathrm{CS}_2$$

The decomposition occurs in aloali ore medium.

Reaction between ammonium sulphide and CS2 with formation of ammonium trithiocarbonate:

$$(\mathrm{NH}_4)_2\mathrm{s} + \mathrm{cs}_2 - - \rightarrow (\mathrm{NH}_4)_2\mathrm{cs}_3$$

This product may give red colour to the solution of the NHADIC.

Decomposition of the ethylene-monothiocarbamic acid to ethylene-thiourea

This dangerous reaction can be avoided operating in alcali ore medium and with an excess of CS<sub>2</sub>.

Partial decomposition of the NH<sub>4</sub>DTC by ammonia and formation of the B-isothiocyanoethylammoniumcarbamate:

$$CH_2 - NH - C - SNH_4 + NH_3 - - \rightarrow CH_2 - NH - C - SNH_4 + (MH_4)_2 = CH_2 - NH - C - SNH_4 + (MH_4)_2 = CH_2 - N = C = S$$

Large excess of HN, should be avoided during the reaction.

#### Maneb

Maneb is the manganese salt of the ethylene-biedithiocarbamic acid.

#### Main reactions

See under zineb.

The precipitation occurs by reaction of NHADTC and a manganese salt:  $\begin{array}{c} -\operatorname{SNH}_4 + \operatorname{MnSO}_4 - - \Rightarrow \begin{array}{c} \operatorname{CH}_2 - \operatorname{NH} - \overset{\circ}{\operatorname{C}} - \operatorname{S} \times \operatorname{Mn} + (\operatorname{NH}_4)_2 \operatorname{SO}_4 \\ \operatorname{CH}_2 - \operatorname{SNH}_4 \end{array}$ 246 151 265 132

The by-product is again ammonium sulphate.

#### Side reactions

See under zineb.

and 2.5% zino.

Main reactions

See under sineb.

The precipitation cocurs by reaction of NHADTC and manganese/sinc salts to form the complex

#### Side reactions

See under sineb.

- 12 -

#### Precipitations of maneb

#### Mancoseb

Manoozeb is a complex of sinc and maneb containing about 205 manganese

Precipitation of mancoseb

$$-S - \frac{C}{S} - \frac{M}{2} - \frac{M}{2} - \frac{M}{2} - \frac{C}{S} - \frac{S}{S} + \frac{S}{2} - \frac{S}{2} + \frac{S}{2} +$$

#### III. RAW MATERIALS

For zineb, maneb and mancozeb production the following raw materials are needed:

Carbon disulphide Ammonia EDA Sulphuric acid Zinc sulphate Manganese sulphate Hexamethylene-tetramine (stabilizer for maneb)

#### Alternatives and motivation for the choice

Carbon disulphide. This product has no alternatives.

<u>Ammonia</u>. Ammonia can be supplied both as anhydrous ammonia and in the form of 20% aqueous solution. In this second case the storage space requirement is bigger, but less expensive than in the first case, because for storing anhydrous ammonia pressurized containers are required. Handling of ammonia solution is less dangerous than handling dry ammonia. It is possible to use NaOH too, but the by-product form using ammonia  $(NH_4)_2SO_4$  is more useful and valuable than Na<sub>2</sub>SO<sub>4</sub>. The recommended choice is aqueous ammonia solution.

EDA. It is possible to work also with a mixture of EDA and higher diamines, like diethylene-diamine, triethylene-triamine, triethylene-poliamine and so on; but the usage of this mixture gives rise to several physical forms of zineb, and it is not suitable in the case of maneb. So, it is suggested that technically pure EDA be used.

<u>Sulphuric acid</u>. There are no problems, because sulphuric acid is required only in small amounts to correct the pH value during the preparation of zineb and is locally available.

Zinc sulphate. This reagent can be used both in solid state and in 12% water solution. In the first case a special equipment is required to prepare the water solution; in the second case the cost of transportation increases. So it is suggested to use the reagent as a solid. In the zineb and maneb synthesis zinc chloride and manganese chloride can be used instead of the sulphates; in this case the by-product is  $NH_4Cl$ . It is felt that it would be more attractive to have  $(NH_4)_2SO_4$  as a by-product because of the possibility to recover it (evaporiting mother liquors) and producing a useful fertilizer. This recovery of ammonium sulphate is not dealt with in this report, but it is recommended, both from an economic point of view and from the point of view of waste disposal. Therefore, the use of zinc sulphate is recommended instead of zinc chloride.

<u>Manganese sulphate</u>. For this product see the above considerations applied to the zinc sulphate.

<u>Hexamethylene-tetramine</u>. Several products can be used as stabilizer, such as calcium or zinc bromide, alumina, silica gel, calcium sulphate etc. Hexamethylene-tetramine is suggested because it is best tested.

## Specifications for raw materials

#### Carbon disulphide

Distilled liquid Purity: about 99% Boiling point: 46°-47°C Density: 1.265 at 20°C Residue to evaporation: max. 50 ppm H\_S: absent

## Apponia water solution

Liquid Purity: about 20% Density: 0.92 at 20°C

#### EDA

```
Liquid

Purity: 98-99%

Melting point: 9°-11°C

Boiling point: 115°-119°C

Density: 0.89 - 0.90 at 20°C

Flash point: 40°C
```

## Sulphuric acid (water solution)

Liquid Purity: 30% Density: 1.22 at 20°C

#### Zinc sulphate

```
Solid
Formula: ZnSO<sub>4</sub>·7H<sub>2</sub>O
Purity: 98-99%
Impurities: Na 1%; calcium, iron, arsen, lead, manganese, less than 0.5%
Particle size: 0.5 mm max.
```

#### Manganese sulphate

```
Solid
Formula: MnSO<sub>4</sub>•H<sub>2</sub>O
Purity: 98-99%
Impurities: calcium, iron, arsen, lead, sinc, less than 0.5%
```

#### Hexamethylene-tetramine

Pure grade

#### Specifio raw material requirements

In table 4 the stiochiometric figures for zineb and maneb are reported, in table 5 the actual raw material requirements for one ton product are listed.

Table 4. Stoichiometric raw material requirements per ton of product

Raw material								
	<b>-</b>	h	Ammonia		ZnSOA		MinSOA	
Product	cs <sub>2</sub>	100%	As 20% solution	EDA	Dry	7н <sub>2</sub> 0	Dry	Ав 1H <sub>2</sub> 0
Zineb	0,550	0,123	0.615	0.217	0.585	1.041	-	-
Maneb	0.573	0,128	0.64	0.226	-	-	0.569	0.636

Raw material	<sup>C3</sup> 2	Amm	onia	EDA	Sul	p <b>huric</b> acid	Zi sulp	nc hate	M sulp	n hate	• Stabilizer
Product		100%	As 20% solution		98%	As 30, solution	Dry	Ав 7Н <sub>2</sub> 0	Dry	Ав 1H <sub>2</sub> 0	
Zineb	0.600	0.130	0.650	0.235	0.032	0.104	0.600	1.070	-	-	_
Maneb	0.635	0 <b>.</b> 135	0.675	0.245	· -	-	-	-	0.570	0.638	0.03
Manocozeb	<b>0.67</b> 5	0.142	0.710	0,253	-	-	0.073	0.130	0.536	0.600	) _

Table 5. Specific raw material requirements per ton of product

#### Sources and prices of raw materials

A survey has been made on the sources of raw materials needed for zineb. maneb and mancozeb production.

<u>Carbon disulphide</u>. This raw material is produced in Turkey by Sümerbank at Gemlik, but only for captive use. The quantity needed is about 1,700 t/year. The international price is about \$0.22 per kg. Other major producers (for example) are Stauffer Chem. Co. (USA), PPG Industries (USA), Baker J.T. Chem. Co. (USA), FMC Corp. (USA), Snia Viscosa (Italy).

<u>Ammonia</u>. It will be produced in Turkey by Azot Sanayii at Gemlik, within one year. In Turkey other producers use ammonia for fertilizer plants. The quantity needed is about 380 t/year (100% basis). The price is about LT 2.8/kg (100% basis).

EDA. This raw material is not produced in Turkey. The quantity needed is about 700 t/year. The international price is about \$1.4 per kg. The main producers are Montedison (Italy), Dow Chem. (USA), Union Carbide (USA), BASF (Federal Republic of Germany).

<u>Sulphuric acid</u>. It is produced in Turkey by Etibank at Bandirma, with a capacity of 120,000 t/year. The quantity needed is about 20 t/year (98% basis). The price now is LT 2.2/kg.

Zinc sulphate. It is produced in Turkey by Kemal Göknur, Sinai Maddeler at Bandirma. The quantity needed is about 530 t/year (100% basis). The international price is about LT 5.5/kg (100% basis). Other producers (only as an example) are: Ashland Chem. Co. (USA), United Mineral and Chem. Co. (USA), Sherwin-Williams Ch. Div. (USA), Zindler (Italy), Hoechst (Federal Republic of Germany).

<u>Manganese sulphate</u>. It is not produced now in Turkey, but if the demand will increase there is a possibility to produce it at Antalya or Bandirma. The quantity needed is about 1,120 t/year (100% basis). The international price is about \$0.4/kg. Producers (only as an example) are Diamond Shamrock (USA), United Mineral and Chem. Co. (USA), Hoechst (Federal Republic of Germany).

<u>Hexamethylene-tetramine</u>. It is produced in Turkey by Karbokimya Endustrive Ticaret AS. at Istanbul. The quantity needed is about 10 t/year. The price is about LT 30/kg.

#### IV. THE MANUFACTURE OF ZINEB, MANEB AND MANCOZEB

# NH4DTC plant

The plant has been considered for the continuous manufacturing of a water solution of the  $NH_4$ DTC, which is the basic intermediate for the metal salts of DTC. The plant has to be considered a multipurpose plant, which could produce other DTC, if necessary, by changing some raw materials (for example by using NaOH instead of ammonia it is possible to produce nabam, another member of the DTC family). See annex I for the flow-sheet for the continuous manufacturing of the  $NH_4$ DTC water solution.

#### Precipitation of zineb, maneb and mancozeb

This section of the plant has been studied for the continuous manufacturing of metal salts of DTC, starting from the aforesaid NH<sub>4</sub>DTC water solution. Its work-plan should be as follows (based on figures of 1984 demand):

- 87 days/year using  $ZnSO_4$  to produce zineb
- 37 days/year using  $MnSO_{\Lambda}$  to produce maneb
- 176 days/year using  $MnSO_4$  and  $ZnSO_4$  to produce mancozeb

The plant has a high flexibility, so the quantities of DTC may be changed according to the market requirements. The flow-sheet of the continuous manufacturing of zineb, maneb and mancozeb is also shown in annex I.

# NH<sub>4</sub>DTC production process

 $NH_4DTC$  is manufactured in aquaous solution by a continuous reaction of  $CS_2$ , EDA and ammonia. The main equipment consists of three reactors (total utilized volume 3,400 litres) set up at descending levels and joined through side tubes set near the top of each vessel. In the first of these reactors the following reagents are introduced at the same time:

CS<sub>2</sub>, 202 1/h Water, 205 1/h EDA, 115 1/h 20% ammonia, 321 1/h The right ratio among the reagents, pH, temperature, stirring and contact time must be strictly controlled. The contact time is arrived at by dividing the total useful reactor volume by the total reagent's volume per hour.

The liquid product which flows through the side-tube of the third reactor is continuously transferred into a static liquid/liquid separator, where the unreacted  $CS_2$  is collected and recycled to the process.

The upper layer, through all intermediate storage vessel and a pump, is continuously transferred into a heat-exchanger and a stripping column where some residual  $CS_2$  is eliminated by an inert gas stream. The product coming out from the bottom of the column consists of NH<sub>4</sub>DTC water solution with the following properties:

NH<sub>4</sub>DTC: 45-47**%** pH: 8-8.5 D<sub>20</sub>: 1.165-1.169

The productivity of the plant is 860 l/h of  $\text{NH}_4 \text{DTC}$  water solution. This amount corresponds to about 2.8 kg of  $\text{NH}_4 \text{DTC}$  (100%) per each litre of reactor in 24 hours. For the required 1984 DTC production this section of the plant must work about 300 days/year.

#### Zineb production process

Zineb is manufactured in aqueous medium by a continuous reaction between  $NH_4DTC$  and  $ZnSO_4$ . The  $ZnSO_4$  water solution is prepared in a suitable vessel in which the salt is dissolved in water or in mother liquors of zineb washings, the amounts of water and  $ZnSO_4$  must be exactly controlled.

The precipitation of zineb takes place continuously in a reactor (total utilized volume 2,450 litre) equipped with a side tube set near the top of the reactor. The following reagents are introduced at the same time in a continuous way:

NH<sub>4</sub>DTC water solution, 656 1/h ZnSO<sub>4</sub> water solution 12%, 1,760 1/h Sulphuric acid 30%, 28 1/h The right ratio among the reagents, pH, temperature, stirring and contact time (1 h) must be exactly controlled.

The slurry of zineb and mother-liquors flow through the side tube into a second reactor, which has the same shape and volume as the first, in which the amorphous zineb's particles change their physical properties to crystalline. The slurry coming out from this reactor is continuously filtered in a rotary vacuum filter, in which a large part of the mother liquor is removed.

The composition of the slurry is roughly as follows:

Before firs	t filtration	After	first filtration	1
Zineb	14%	Cake:	Zineb	42
$(NH_4)_2 SO_4$	8 <b>%</b>		(NH <sub>4</sub> ) <sub>2</sub> 50 <sub>4</sub>	5%
ZnS04	0.1%		ZnS04	not deter-
By-products	0.9%		By-products	2 <b>%</b>
Water	7 <b>7</b> \$		Water	51 <b>%</b>
		Nother	-liquors:	10.5%
			$(\mathbf{NH}_{4})_{2}$ so <sub>4</sub>	
			Others	0.5%
			Water	89%

While the mother-liquors could be sent to the recovery of  $(NH_4)_2SO_4$ , the cake is continuously diluted with water in a screw-conveyor and filtered again in a second rotary vacuum filter, which has the same shape and capacity as the first.

The composition of the product is roughly as follows:

Before second filtration			After second filtration		
Zineb	15%	Cinice :	Zineb	45.2%	
(MH <sub>4</sub> ) <sub>2</sub> 90 <sub>4</sub>	25		$(MH_4)_2 SO_4$	0.3%	
By-products	1%		Others	1.5%	
Water	825		Water	53%	
		Nother-liquors:	Water	98%	
			Salts	26	

The cake of zineb is continuously sent by a belt-conveyor into another equipment, in which water is added (or recycled mother-liquors) so that a new slurry is formed, whose composition is as follows: zineb 30%, water 70%. This last slurry is dryed in a spray-dry special equipment and zineb is collected.

The dried technical grade zineb has the following average composition:

Before filtration

The capacity of the plant is about 375 kg of zineb per hour. This amount corresponds to about 3.7 kg of technical grade zineb per each litre of reactor in 24 hours. For the required 1984 zineb production the plant shall work about 87 days/year.

#### Maneb production process

Maneb is manufactured in aqueous medium by a continuous process between  $NH_4DTC$  and  $NnSO_4$ . For details about the equipment for precipitation and volumes see under zineb process. The reagents are:

NH<sub>4</sub>DTC water solution, 885 1/h MnSO<sub>4</sub> water solution 16.2%, 1,530 1/h (Neither sulphuric acid (30%) nor the second filtration are needed).

The composition of the slurry coming into the filter is roughly as follows:

After filtration

Naneb	18 <b>% Cake :</b>	Maneb	71\$
$(MH_4)_2 SO_4$	8.5 \$	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1%
Minso <sub>4</sub>	0.5%	Water	28%
Water	73% Nother-liquors:	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	11.5%
		MinSO	0.4%
		Maneb	0.1%
		Water	88%

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While the mother-liquors could be sent to the recovery of  $(NH_4)_2SO_4$ the cake is continuously diluted with water to which a stabilizing agent is added, so that the composition of the slurry becomes: maneb 30%, stabilizer 1%, water 69%. After spray drying the technical grade maneb has the following average composition:

Maneb	92%
Water	0.5%
$(\mathrm{NH}_4)_2 \mathrm{SO}_4$	1%
Others	6.5%

The output of the plant is about 490 kg of maneb per hour. This amount corresponds to about 4.8 kg of technical grade maneb per litre of reactor in 24 hours. For the projected 1984 maneb requirement the plant must work about 37 days/year.

#### Mancozeb production process

On the basis of the information supplied by UNIDO and other sources, but not by personal experiences, mancozeb can be manufactured by a similar procedure. The reagents are as follows:

NH<sub>4</sub>DTC water solution, 862 1/h ZnSO<sub>4</sub> water solution 12%, 255 1/h MnSO<sub>4</sub> water solution 16.2%, 1,340 1/h

For filtration and drying see under maneb process.

The output of the plant has been considered to be about 472 kg of mancozeb per hour. This amount corresponds to about 4.6 kg of technical grade mancozeb per each litre of reactor in 24 hours. For the projected 1984 mancozeb requirement the plant must work about 176 days/year.

#### V. PLANT LOCATION

The selection of a suitable location for the plant should take into account the following considerations:

Availability of utilities, services (electricity, water, steam) and effluent disposal facilities Proximity to markets, such as the formulation plants in which DTC are formulated Other pesticide factories Price of land Availability of raw materials and labour

As far as this last item is concerned, for a DTC production unfortunately a large part of raw materials has to be imported, since some are not in local production now. So, the availability of raw materials has been considered only as a future possibility, assuming that the most important raw materials could become available with the expansion of the  $CS_2$  Sumerbank plant (Gemlik) and the creation of an EDA plant, starting from dichlorethan, now produced by Organic Chemical Company (Gemlik). This last alternative is highly recommended.

On the basis of the aforesaid considerations it was felt that the DTC plant should preferably be located in the north-west of the country, close to the izmit industrial area. In this choice an important consideration was given to the suggestion of this area for a 2,4-D plant, by a UNIDO study. It was felt that it would be more convenient for the Turkish Government to establish a single factory, in which not only DTC, but various pesticides could be manufactured. In this case services for waste disposal, training of workers, chemical and analytical laboratories, social and other services could be provided at the same time and with the same effort.

Taking into account all these factors the expert recommends the ohoice of the Orhangasi area for the DTC plant.

This area is close to the Iznik lake. Obviously water is very conveniently available from the lake; as far as power is concerned there is a high tension transmission line passing through the area and already supplying power to an iron foundry located in this region. Mother-liquors can be discharged into a channel which carries overflow from the lake into Marmara sea. It is important that waste waters of the DTC plant don't contain dangerous contaminating materials. The main by-product is  $(NH_4)_2SO_4$ , which can be recovered only by evaporating the water, followed by crystallization. This procedure is highly recommended, both for obtaining a useful fertilizer and for decreasing the waste disposal problems. The price of the land in this region also seems to be quite reasonable at about LT 200 per m<sup>2</sup>. From all these considerations Orhangazi area seems to be very well situated for locating a DTC plant.

#### VI. PLANT MANAGEMENT

The capacity of the plant has been planned for a continuous manufacturing of DTC based on the projected 1984 demand and over 300 working days. The initial operating capacity has been planned on the basis of the 1980 demand, that is zineb 525 t, maneb 300 t and mancozeb 1,300 t. (Total 2,125 t of DTC, i.e. 65% of the planned capacity.)

The work will be organized on three shifts, five days/week basis. Table 6 shows the labour requirements and cost. The figure below shows the organizational chart of the plant.

Post title	Number	Qualifications	Monthly salary (LT)	Total monthly expenses (LT)
Management				
Plant general manager	1	Senior chemical engineer	18 <b>000</b>	18 <b>00</b> 0
Plant production manager	1	Chemical engineer	15 000	15 000
<b>Per</b> sonnel and administration	1	Administrative	15 <b>000</b>	15 000
Plant maintenance manager	1	Nechanical engineer	15 <b>000</b>	15 000
Laboratory manage	er 1	Chemistry graduate	8 000	8 <b>000</b>
Head packaging operation	1	Mechanical technologist	8 <b>000</b>	8 <b>000</b>
<b>Assistant</b> to plant maintenance manager	<u>1</u>	Nechanical technologist	8 <b>000</b>	<u>8 000</u>
Subtotal	7			87 000
Supervision				
Analysts	2	Skilled workers	6 000	12 000
Assistant to packaging	1	Skilled workers	6 000	6 <b>000</b>
Shifts supervisor	ъ <u>3</u>	Skilled workers	6 000	<u>18 000</u>
Subtotal	6			36 000

Table 6. Labour requirements and cost

Table 6 (continued)

Post title	Number	Qualifications	Monthly salary (LT)	Total monthly expenses (LT)
Direct labour				
Packaging	3	Workers	4 800	14 400
NH4DTC	3	Workers	4 800	14 400
Precipitation	3	Workers	4 800	14 400
Filtration	3	Workers	4 800	14 400
Drying	3	Workers	4 800	14 400
<b>Rev-material</b> discharge	2	Workers	4 800	9.600
Maintenance, shifts	3	Workers	6 000	18 000
General mainte- nance	2	Workers	6 000	12 000
Leave/sickness				
COVER	_2	Workers	4 800	9 600
Subtotal	24			121 200
Total	37			244 200



ORGANIZATIONAL CHART

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# VII. ECONOMIC CONSIDERATIONS

#### Cost of raw materials

In table 7 the cost of raw materials for 1 t zineb, 1 t maneb and 1 t mancozeb production is reported. (The quantities of raw materials needed for 1 t production have been reported in table 5.) For zineb production the foreign raw materials cost is 65% of the total raw materials' cost. For maneb production the cost of foreign raw materials is 90% of the total raw materials' cost. For mancozeb production the cost of foreign raw materials is 94% of the total raw materials' cost.

	Cost o	f raw	Cost	of raw ma	aterials	for prod	uction of	
		TIALS	Zinet	)	Ma	reb	Manco	seb
<b></b>	LT/kg	\$/kg	LT/t	\$/t	LT/t	\$/'t	LT/t	\$/t
cs <sub>2</sub>	4.23	0,22	2 538	131.84	2 686	139.53	2 855	148.31
Ammonia.	2.8	0.14	364	18.91	378	19.63	397	20,62
EDA	27	1.40	6 345	329.61	6 615	343.63	6 831	354.85
H <sub>2</sub> S04	2.2	0.11	704	36.57	-	-	-	-
ZnSO4	6.5	0.34	3 900	202.59	-	-	474	24.62
Mnso <sub>4</sub>	7 <b>•7</b>	0.40	-	-	4 389	228	4 127	214.38
Hexamethylene- tetramine <u>a</u> /	30	1.56			900	46.75		
Total			13 851	719.52	1 <b>4 96</b> 8	777.54	14 684	762.78

Table. 7 Cost of raw materials for zineb, nameb and manooozeb production

Available in Turkey.

#### Cost of utilities

The consumption and the costs of the utilities for the DTC production is given in table 8.

Utilities	Quantity required	Unit price (LT)	Cost per ton of DTC (LT)
Electricity	0.6 kWh/kg	0.66/kWh	396
Water	$0.6 \text{ m}^3/\text{kg}$	0.55/m <sup>3</sup>	330
Steam	6 kg/kg	0.19/kg	1 140
Fuel	$0.3 \text{ m}^3/\text{kg}$	10/m <sup>3</sup>	600
Nitrogen	0.01 m <sup>3</sup> /kg	15/m <sup>3</sup>	150
K-refrigeration	0 <b>.</b> 36/kg	0.7/kg	_250
Total			2 8 <b>66</b>

Table ö. Cost of utiliti	Table	8.	Cost	of	utilitie
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#### Cost of direct labour and supervision

The cost of direct labour and supervision, per ton of DTC is reported. For the monthly labour expenses see table 6.

At 1980 production level of 2,125 t/year the costs will be as follows:

<u>LT</u>

Yearly direct labour cost	1,454,400
<b>Yearly supervision</b> cost	432,000
	1,886,400
Welfare benefits (30%)	565,920
Total	2,452,320

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Direct labour and supervision cost per ton of DTC will be LT 1,154 (2,452,320 ± 2,125).

#### Direct cost of production

In table 9 the direct cost of production per ton of zineb, maneb and mancozeb is reported.

		(Liyton)		
Product	Raw materials	Utilities	Direct labour and supervision	Total
Zineb	13 851	2 866	1 154	17 871
Maneb	14 968	2 866	1 154	18 988
Nancozeb	14 684	2 866	1 154	18 <b>704</b>

Table 9. Direct cost of production of zineb, maneb and mancozeb (LT/ton)

#### Working capital calculations

	LT
2 months of salaries $(2 \times 244,200)$	488,400
3 months of raw materials	7,712,800
1 month finished products <sup>b/</sup>	4,500,000
	12,701,200

A Raw materials for:

<u>b</u>/

Zineb 525 t $(13,851 \times 525)$ Maneb 300 t $(14,968 \times 300)$ Mancozeb 1300 t $(14,684 \times 1,300)$	7,271,775 4,490,400 19,089,200
Total yearly (1980)	30,851,375 4 = 7,712,843
Yearly production:	
<b>Z</b> ineb 535 t	
Maneb 300 t	
Mancozeb 1.300 $t$	

Total 2,135 : 12 = 177 t/month x 25.000 LT/t(average cost for 3 producta) = about 4,500,000

# Fixed capital investment calculations

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1.	Installed plant cost estimation:	LT
A.	Cost of equipment at site	
	(a) Cost of local equipment	29,000,000
	(b) Cost of imported equipment	14,726,000 (\$765,000)
	(c) Duties and customs (75% on (b))	11,044,700
	(d) Inland cost of transportation (1% on (a) + (b))	437,200
	Total	55,207,900
B.	Cost of piping and instrumentation:	
	20% on total A	<u>11,041,580</u>
	Total	11,041,580
C.	Cost of projection and installation:	
	(a) Projecting: 10% on total A	5,520,790
	(b) Installation: 20% on total A	11,041,580
	Total	16,562,370
	Total $(A + B + C)$	82,811,850
2.	Cost of buildings	
	Plant, laboratory, offices, warehouses, social facilities etc.	8,5 <b>00,000</b>
3.	Cost of land	
	$6,000 \text{ m}^2$ at LT 200/m <sup>2</sup>	1,200,000
	Total fixed capital investment	92,511,850 (\$4,805,810)
	Indirect cost of production	

Table 10 shows the indirect cost of production.

# Total cost of production

Table 11 gives the total cost of production.

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Table 10. Indirect cost of production (LT)

	, I		ਲ	st of 1 t DTC		
tea	Yearly cost	1980 (production 2,125 t)	1981 (production 2,450 t)	1982 (production 2,750 t)	1983 (production 2,925 t)	1984 (production 3,250 t)
<pre>bintenance</pre>	2 208 316	1 039	901	303	755	619
nsurance						
1.5% of installed plant cost	828 118	<b>6</b> 92	338	301	283	254
1.5% of cost of buildings	127 500	60	52	46	43	66
<b>lant</b> depreciation						
10% of installed plant cost	t 5 520 790	2 598	2 253	2 001	1 887	1 698
wildings depreciation						
3% of cost of buildings	255 000	120	20	92	87	78
interest on capital						
12% long term loan interest	5 550 711	2 612	2 265	2 <b>01</b> 8	1 897	1 708
12% on working capital	1 524 144	717	622	554	521	469

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table 10 (continued)

	Veel-		8	set of 1 t Dro		
Ita		<b>1980</b> (production 2,125 t)	1981 (production 2,450 t)	1982 (production 2,750 t)	1983 (production 2,925 t)	1984 (production 3,250 t)
Bunagement overhead						
Yearly malaries of management	1 044 000	164	426	379	357	ĸ
20% expenses on management salaries	208 000	86	8	<u> </u>	17	3
Indirect cost of production total	17 266 579	8 124	7 046	6 276	5 901	5 310

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a/ Based on 50% of the total fixed capital invostment.

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		ς-	-,		
ineb	1980 (production 525 t)	1981 (production 600 t)	1982 (production 675 t)	1983 (production 725 t)	1984 (production 800 t)
Direct cost of produc- tion	17 871	17 871	17 871	17 871	17 871
Indirect cost of production Total	<u>8 124</u> 25 995	<u>7 046</u> 24 917	<u>6 276</u> 24 147	<u>5 901</u> 23 772	<u>5 310</u> 23 181
aneb	1980 (production 300 t)	1981 (production 350 t)	1982 (production 375 t)	1983 (production 400 t)	1984 (production 450 t)
Direct cost of produc- tion	18 988	18 988	18 988	18 988	18 988
Indirect cost of production	8 124	<u>7 046</u>	6 276	<u>    5   901</u>	<u> </u>
Total	27 112	26 034	25 264	24 889	2 <b>4 29</b> 8
Manoozeb	1980	<b>19</b> 81	1982	1983	1984

(production

1.700 t

18 704

6 276

24 980

(production (production

2 000 t)

18 704

5 310

24 014

1.800 t)

18 704

5 901

24 605

Table 11.	Total cost of production per ton of zineb	,
	maneb and mancozeb	
	(LT)	

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Zine

Mane

Direct cost of production

Indirect cost of

production

Total

#### Imported DTC prices

(production)

1.500 t

18 704

<u>7 046</u>

25 750

According to the information of TZDK the average c.i.f. imported prices for zineb, maneb and mancozeb in 1977 were as follows:

Zineb, \$765 per ton (LT 14,726) Maneb, \$1,632 per ton (LT 31,416) Mancozeb, \$1,960 per ton (LT 37,730)

(production

1,300 t)

18 704

8 124

26 828

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(The imported prices of the technical grade Mancozeb (active ingredient) has been estimated taking into account the price of the 80% formulated fungicide (about \$1,600 per ton) and considering the value of the formulating agents 1/10 of the active ingredient's value.)

#### Profitability of the investment

Return on investment against imported prices for 1980 is as follows:

- Zineb: $525 t \ge LT 25,995 = LT 13,647,375$  (total cost of production) $525 t \ge LT 14,726 = LT 7,731,150$  (total sales return)Gross lossLT -5,916,225
- Maneb:
   300 t x LT 27,112 = LT 8,133,600 (total cost of production)

   300 t x LT 31,416 = LT 9,424,800 (total sales return)

   Gross profit
   LT 1,291,200
- Mancozeb:1,300 t x LT 26,828 = LT 34,876,400 (total cost of production)1.300 x LT 37.730 = LT 49,049,000 (total sales return)Gross profitLT 14,172,600

Overall profitability: -5,916,225 1,291,200 <u>14,172,600</u> LT 9,547,575

1980 return on investment: <u>9,547,575</u> x 100 = 10.32% 92,511,850

A return on investment against imported prices for 1984 is as follows:

- Zineb: 800 t x LT 23,181 = LT 18,544,800 (total cost of production) 800 x LT 14,726 = LT 11,780,000 (total sales return) Gross loss LT -6,764,000
- Maneb: 450 t x LT 24,298 = LT 10,934,100 (total cost of production) <u>450 t x LT 31,416 = LT 14,137,200</u> (total sales return) Gross profit LT 3,203,100
- Mancozeb:2,000 t x LT 24,014 = LT 48,028,000 (total cost of production)2.000 t x LT 37.730 = LT 75,460,000 (total sales return)Gross profitLT 27,432,000

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Overall profitability: -	6,764,000 3,203,100 7.432,000
1084 motures on transformed	23,871,100
1704 return on investmen	x 100 = 25.87 92,511,850

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#### Foreign exchange savings

Case of a local production:	Dollars
Foreign equipments cost	765,000
Pive years 12% interest	459,000
Five years foreign raw materials cost	8,818,327
Total foreign exchange to be paid	10,042,327
Case of finished products imports	
Five years zineb (3,325 t x \$765)	2, 543, 625
Five years maneb (1,875 t x \$ 1,632)	3,060,000
Five years mancozeb (8,300 t x \$1,960)	16,268,000
Total foreign exchange to be paid	21,871,625

Foreign exchange. savings in the case of a local production:

21,871,625 -10,042,327 \$11,829,298 for the 1980-1984 period

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#### VIII. CONCLUSIONS AND RECOMMENDATIONS

#### Conclusions

From this feasibility assessment the following main conclusions can be drawn.

1. The domestic demand of DTC fungicides is expected to increase from 680 t (1976) to 3,250 t (1984) and a local DTC production will encourage the enlargement of the use owing to a wider availability of the products.

2. The envisaged production plant is suitable to produce different DTC fungicides by changing only some raw materials: the main intermediate (NH<sub>4</sub>DTC) is the same for zineb, maneb and mancozeb. The plant could be considered a multipurpose one, because of the possibility of producing other DTC, if required. Idle periods should be avoided, so that maximum advantage and cost benefit could be obtained from the continuous process design.

3. Main raw materials for manufacturing DTC have to be imported (about 65% for zineb, 90% for maneb, 94% for mancozeb).

4. As far as the process is concerned, there are several producers who could supply the know-how: no problems of royalties for patents are likely to arise.

5. A suitable plant location has been suggested in the north-west of Turkey, near Orhangazi area, not very far from some formulation plants. The cost of the land in the proposed area is about LT 200 per  $m^2$ .

6. The plant management has been considered on a basis of 300 working days: the initial operating capacity (1980) is about 65% of the planned capacity. Three shifts for five days/week have been suggested for the first year of production.

7. The total cost of production on 1980 basis is roughly:

Zineb LT 26,000 per t (selling price LT 14,700 per t) Maneb LT 27,000 per t (selling price LT 31,400 per t) Mancozeb LT 27,000 per t (selling price LT 37,000 per t)

8. The economic analysis has pointed out that only the zineb production doesn't show profitability, owing to the very low selling price of imported product. In spite of the estimated loss on zineb production, the overall return on investment is about 10% at the start-up time, and will reach 25% when the design capacity will be reached (1984). 9. In the period 1980-1984 under consideration a local DTC production shows a foreign exchanges savings of about \$12,000,000.

#### Recommendations

On the basis of the above conclusions it is recommended:

1. To proceed with the implementation of the plant establishment and with the preparation of tender specifications.

2. To consider the possibility of establishing a DTC factory in the same area where 2,4-D will be manufactured. Considerable advantages will be obtained from an economic point of view as far as the common management, laboratory and other services are concerned.

This suggestion considers a long term possibility of manufacturing other pesticides, besides DTC and 2,4-D, for the future requirements of Turkish agriculture.

The purchase of the suggested area should take into consideration a potential expansion in manufacturing activities.

3. Foreign raw materials have a great influence on the foreign exchange requirements of DTC production. It is suggested that studies be carried out on an expansion of the existing CS\_plant and the establishment of an EDA local production plant using locally available dichloroethane as raw material.

4. It is strongly recommended to set up a training programme for technical people, especially devoted to organic technology required in DTC production.

5. In a future development of the DTC project it is suggested to consider the realization of  $(NH_4)_2SO_4$  recovery unit.

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DRAWINGS OF THE PLANT





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DRAWINGS OF THE PLANT







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#### Annex II

# PROCESS EQUIPMENT COST SUNMARY AND LIST

	Local equipment cost (LT)	Imported equipment cost	Total cost (LT)
Storage	20 800 000	_	20 800 000
NH <sub>A</sub> DTC plant	3 100 000	<b>4</b> 5 <b>00</b> 0	3 966 000
Precipitation plant	5 100 000	720 000	18 960 000
	29 000 000	765 000	43 726 000
			(\$2 271 500)

# Process equipment cost summary

Local equipment, 66%

Imported equipment, 34%

# Equipment list

# Liquid raw materials storage

	Local (LT)	Imported (8)
20 <b>% amm</b> onia tanks, steel, 150,000 l (n.3)	6,500,000	-
EDA tanks, steel, 100,000 l (n.3)	4,200,000	-
H <sub>2</sub> SO <sub>4</sub> tank, steel, 8,000 1	100,000	-
CS <sub>2</sub> tanks, steel, underwater, 200,000 1 (n. 2	3) <u>10,000,000</u>	_
	20,800,000	-
20% ammonia feed tank, steel, 1,200 1	17.000	-
2079 Ammonia feed tank, steel, 1,200 1	17,000	-
EDA leed tank, steel, 500 1	7,000	-
CS <sub>2</sub> feed tank, steel, 1,000 l	14,000	-
Jacketed reactors, (stirrer, motor), stainle	88_	
steel, 1,500 l (n.3)	-	45,000
Condensers, steel (n.3)	160,000	-

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Liquid/liquid separator, steel, 1,500 1	21,000	-
Storage vessel, steel, 1,500 l	21,000	-
Heater exchanger, steel, 900 1/h	200,000	-
Stripping column, Rashig 700 1	20,000	-
Heater exchanger, steel, 100 l/h	150,000	-
Jacketed storage vessel, steel, 25,000 1	350,000	-
Refrigeration equipment	2,000,000	-
Pumps	140,000	
	3,100,000	45,000

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# Precipitation plant

Feed vibrator, steel, 500 1	-	30,000
Elevators and belt conveyers (n.4)	400,000	-
Jacketed reactor (stirrer, motor), steel, 3,000 1	150,000	-
Feed tank, steel, 200 1	3,000	-
Jacketed reactor (stirrer, motor), stainless- steel, 3,000 1	-	30 <b>,000</b>
Jacketed reactor (stirrer, motor), stainless- steel, 100 l	-	1,000
H <sub>2</sub> SO <sub>4</sub> feed tank, PVC, 20 1	2,000	-
Reactor (stirrer, motor), stainless-steel, 3,000	L -	29,000
Rotary vacuum filter (package unit) 0.5 t/h (n.2)	) –	130,000
Pumps, belt screw conveyers	245,000	-
Reactor (stirrer, motor), steel 500 1	100,000	-
Spray-drier (package unit) 0.5 t/h	-	400,000
Finished products tanks, steel, 100,000 1 (n.3)	4,200,000	-
Packaging unit	<b></b>	100,000
	5,100,000	720,000



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