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METHYL PARATHION
AN INDUSTRY PROFILE[1/]

by

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CONTENTS

S U M M A R Y

Methyl Parathion belonging to the organo-phosphorous group of pesticides is one of the widely used insecticides due to its rapid knock-down effect and relatively lower application costs. However, the use of Parathions is banned or restricted in some countries. In some cases, use of Ethyl Parathion has been banned but use of Methyl Parathion has been allowed. Again, in some cases, due to higher Toxicity hazards at the time of application, (even in the case of Methyl Parathion) while use of dusts is allowed, the use of emulsifiable concentrates has been restricted to Government supervised programmes as in India. Notwithstanding its toxicity, it is one of the most popular insecticides in most parts of the world.

Parathion requirements for Philippines, Thailand and Indonesia in 1975 were around 474 M.T. as reported by Messrs. C. Pope and A.J. Hagen (UNIDO/ID.150 - UNIDO/FAO Prefeasibility Survey of pesticide production and use in certain countries). Its use in India is around 1200 T.P.A. and installed capacity of 1700 TPA. Manufacturing facilities do not exist in other developing countries of the area.

Major basic raw materials for manufacture of Methyl Parathion are Phosphorous Pentasulphide, Methanol, Toluene, Thionyl Chloride, Phenol, Nitric acid and Sulphuric acid. The manufacturing process involves three steps :

1. Preparation of Dimethyl Thiophosphoryl Chloride;
2. Preparation of Sodium - p - Nitrophenate; and
3. Condensation of Dimethyl Thiophosphoryl Chloride and Sodium - p - Nitrophenate to give Methyl Parathion.

The route for production of Methyl Parathion involves utilisation of dimethyl thiophosphoric acid which is a starting material for a number of organophosphorous compounds and is a most desirable route especially should it be decided to set up an organo-phosphorous pesticides complex to manufacture other products also.

Capital cost for a 500 T.P.A. plant (which is of an economic size) under Indian conditions works out to be Rs.11.43 million. A detailed list of equipments, construction costs, offsite facilities etc. is provided in this report. Similarly, details of manpower requirements, maintenance and depreciation costs, utility costs etc. are provided. Also, the information on working capital is provided. The cost of production works out to be around Rs.28,500/M.T.

The major by-products, which are saleable, are Hydrochloric acid (30%), sodium hydrogen sulphide, O - Nitrophenol and sodium chloride - the last is not economical to recover.

Some of the effluents even can be recovered as saleable products; others neutralized or incinerated. The disposal of effluents should not pose a major problem.

The safety and environmental considerations in case of Parathion manufacture and use is of great importance. Incidents of explosion in manufacture and over-exposure in handling, storage and application leading to fatalities have been reported and as such extraordinary precautions are needed from the manufacturing stage to end-use of the product.

Specifications for the end-product as laid down by W.H.O. and Indian Standards Institution (ISI) are provided in the report.

Patents for manufacture of Parathion have expired all-over the world. There are six known manufacturers of Parathion - the two largest being Bayer (W) and Monsanto.

CHEMISTRY & INSECTICIDAL ACTIVITY

Methyl parathion (O,O - Dimethyl - O - p - nitrophenyl phosphorothioate) is an insecticide and an acaricide with broad spectrum of activity but with high mammalian toxicity (LD 50; rats oral 14-24 mg/kg body weight; dermal 67 mg/kg body weight).

Parathion is a high boiling deep brown to yellow liquid which possesses a characteristic odour. Technical grade material has a specific gravity of 1.36 and is soluble in most organic solvents but is slightly soluble in aliphatic hydrocarbons. Its solubility in water is very low (55-60 mg/litre). Parathion is stable to hydrolysis in distilled water, hard water and acid solutions. It is, however, rapidly hydrolysed in the presence of alkaline materials such as lime, sodium hydroxide and lime sulfur etc.

Structural formula

After treatment with parathion, some phytotoxicity to green house crops like cucumber and tomatoes has been observed when emulsions are used. But, if parathion is used as a wettable powder or diluted dusts, phytotoxicity is rarely observed. Other vegetable crops and ornamentals can tolerate quite large doses without any harmful effect.

It has been used most [illegible] for the control of green leaf hoppers, rice borers, [illegible], cut worms, rice case worms, leaf rollers, rice bugs, hairy caterpillars in cereals, spotted boll worms, [illegible], thrips, aphids and mites in cotton, leaf [illegible], aphids, beetles, thrips, leaf miners, [illegible], cabbage [illegible], cabbage worms, fruit worms, mites, [illegible] in vegetables; and [illegible], [illegible] caterpillars, aphids and leaf miners in legume crops.

[illegible] emulsifiable concentrate [illegible], [illegible] powder (15-?%) and dusting powder [illegible].

FORMULATION AND PACKAGING

Methyl Parathion is formulated as emulsifiable concentrates (25-50%), wettable powders (15-25%) and dusting powders (1-2%). Formulation facilities for E.C's and dusting powders exist in many of the countries. However, as mentioned earlier, the dusts should, perhaps, find favour for manufacture due to their lower application hazards.

Emulsifiable concentrates of Methyl Parathion have been used extensively either alone or in combination with other products especially DDT. M. Parathion and DDT combination dusts are also quite popular in many countries especially for cotton pest control. The demand for this product in the developing countries of Asia including India is estimated to be no more than 2,000 TPA. India has an installed capacity for 1,000 TPA and may not be fully utilised due to restricted use under the Insecticides Act. No known restrictions exist in other countries but such prohibition cannot be ruled out in the future. This matter would have to be discussed with country governments and assurances obtained prior to establishment of manufacturing facilities.

DESCRIPTION OF PROCESS FOR METHYL PARATHION

The process of manufacture involves three steps:

(a) Preparation of Dimethyl thiophosphoryl chloride.

(b) Preparation of Sodium p-nitrophenate.

(c) Condensation of Dimethyl thiophosphoryl chloride and Sodium-p-Nitrophenate to give Methyl Parathion.

(a) Preparation of Dimethyl thiophosphoryl chloride.

In the present method of commercial production of Dimethyl thiophosphoryl chloride, phosphorus pentasulphide and methanol are heated in a solvent like toluene and then chlorinated with either chlorine or thionyl chloride.

There are other methods also starting from phosphorous trichloride and dialkyl chlorophosphorothiochloridate which, however, have not found much use. The method described earlier has the advantage of utilising dimethyl dithiophosphoric acid which is a starting material for a number of organo-phosphorous pesticides and thus is most suited for organophosphorous pesticide complex.

(b) Preparation of Sodium-p-Nitrophenate.

Phenol is nitrated in presence of nitric acid and sulphuric acid at a regulated temperature to yield a mixture of p- and o-nitrophenol which are separated by either fractional distillation or steam distillation and converted into sodium salt

by sodium hydroxide. The yield of o-nitrophenol has been achieved to the extent of 90-70%.

(d) Preparation of Methyl Parathion.

There are number of methods which have been used for condensation of dimethyl thionophosphoryl chloride and sodium-p-nitrophenate. This exothermic reaction can be carried out at 90°C to 100°C, when the time required is 5 hours and also at -10°C to +10°C when the time required is 24 hours. The reaction is conducted in liquid phase and the solvent like alcohol, benzene, chlorobenzene, methyl ethyl ketone etc. has been used. Some of the catalysts like copper, potassium bromide, tri ethylamine, tri-n-propylamine, n-butylamine, triethanolamine etc. are known to accelerate the condensation step.

A. The reaction is carried out in a stirred jacketed closed vessel system to get a yield of about 90%. The reaction product mixture may be pumped through a pressure filter to remove gummy impurities and filtrate is separated into aqueous acid oily layer. The oily layer may then be washed with a dilute sodium carbonate solution and the contaminated dimethyl chlorophosphate is removed by steam distillation. After cooling and settling, the organic layer can be dried by heating under vacuum to give the product.

B. A product containing upto 96-98% Methyl Parathion is obtained when the reaction of Dimethyl chlorothiophosphate with p-Nitrophenol is conducted in presence of anhydrous potassium

carbonate in acetone with the use of sufficiently pure starting material. This product for convenience of handling and transportation is diluted with 10-15% xylene.

C. The most important industrial method is the reaction of Dimethyl chlorothiophosphate with p-Nitrophenol in presence of Hydrogen chloride acceptors or with Sodium-p-Nitrophenolate. The reaction is carried out in water in presence of emulsifiers (e.g. ammonium or amine naphthalenes). By the aqueous method, the compound is obtained with 85-90% of the principal product.

Choice Of The Method.

Out of the three condensation methods described above A and C are in common use. Process A, because of the problem of evaporation of organic solvents at the lowest possible temperature (through film evaporation techniques) required to avoid any possible explosions may not be suitable for less industrialised developing country and, therefore, process C becomes a method of choice.

RAW MATERIAL REQUIREMENT PER KG. OF METHYL PARATHION

P_2S_5	0.48
Methanol	0.30
NaOH	0.20
Phenol	0.87
Nitric Acid	0.36
Sulphuric Acid	0.78
Chlorine	0.30
Toluene	0.13
Emulsifier	0.04

UTILITIES

Utility	Specifications	Quantity	Application	Equipment required
Water	Softened to 40-50 ppm of hardness limit	160,000 gpd	For process requirement, scrubbing of effluent gases, bye-product recovery, make up water in cooling towers, boiler feed etc.	i) Cooling tower ii) Cooling water circulating pumps iii) Cooling tower sumps
Steam	10 psig and 35 psig	5 tonnes/day	Required in the process for p-nitrophenol making, methyl parathion and solvent recovery units.	i) Boiler 1.5 tonnes/hr ii) Oil and water storage tank iii) Hydraulic pressure test pump
Power	-	77296 units per day	For main plant, agitators, pumps lighting etc.	400 KVA
Refrigeration	-	50 tonnes	Required at most steps of manufacture	2 Brine units of 25 tonnes/capacity.

CAPITAL COST

		(Rupees in thousands)
1.	Land and land development (20 acre of land)	2000.00
2.	Equipment cost including effluent treatment plant	1980.00
3.	Plant building, civil and structure	800.00
4.	Painting and insulation	300.00
5.	Erection	900.00
6.	Engineers and detailed engineering	2000.00
7.	Commissioning	3000.00
		11980.00

CAPITAL INVESTMENT

A) Plant & Machinery

		(Rupees in thousands)
1)	Phenthoate - Dithiophosphoric acid unit :-	
i)	M.S. glasslined vessel with reflux condenser (500 litres) (1 No.)	300.00
ii)	M.S. batch tank for toluene 200 litres (1No)	0.60
/batch iii)	MS/tank for methanol 600 lts.(1 No)	1.00
2)	Dimethyl chlorothiophosphoric unit :-	
i)	MS glasslined vessel 500 lts. with reflux condenser (2 Nos.)	300.00
ii)	Storage tank lead-lined 7000 litres cap.(1 No)	15.00
3)	Condensation unit:-	
i)	MS glasslined vessel 1000 lts. with reflux condenser (1 No.)	300.00
4)	Sodium-o-Nitrophenate unit:-	
i)	SS reactor 1000 lts. (1 No)	75.00
ii)	Leadlined wash tank 1000 lts.(1 No)	6.00
iii)	MS batch tank for H_2SO_4 200 litres (1 No.)	0.40
iv)	MS-AR brick lined batch tank 500 lts. (1No.)	8.00
v)	SS batch tank for HNO_3 200 lts. (1 No)	4.00
vi)	M.S. distillation unit (1No)	20.00
vii)	SS storage tank p-nitro-phenol (1 No)	20.00
5)	Miscellaneous :-	
i)	For effluent treatment unit	500.00
ii)	Misc. equipment e.g. storage tank, pumps etc.	100.00
iii)	Pipe line fittings etc.	20.00
iv)	Misc. (contingencies)	10.00
B)	Land and building offsite facilities and misc.	15000.00
		17360.00

ESTIMATE OF OFFSITE FACILITIES AND MISC. EXPENDITURE

		(Rupees in thousands)
1.	Water Overhead tank 50M³ construction & water supply	40.00
2.	Power receving and distrubution system including emergency power	2000.00
3.	Water softening plant capacity 25M³/hr	100.00
4.	Air for instrumentation 3 M³/hr	75.00
5.	Refrigeration capacity 50 tonnes	600.00
6.	Cooling tower	400.00
7.	Road piping	350.00
8.	Compound wall and fencing	150.00
9.	Roads as per layout	50.00
10.	Time office, change room and welfare	85.00
11.	Canteen	100.00
12.	Laboratory	255.00
13.	Dispensary	30.00
14.	General Store	65.00
15.	Administration block	450.00
16.	Transport Vehicle	90.00
17.	Security and guard room	30.00
18.	Material Handling equipment	200.00
19.	Storage Underground i) Methanol ii) Toluene	300.00
20.	Caustic soda and sulphuric acid	200.00
21.	Raw material and drum storage	50.00
22.	Fuel oil storage	100.00
23.	Methyl parathion	50.00
24.	Steam generator plant 1.5 tonnes/hr	350.00
25.	Misc. i) Preliminary	200.00
	ii) Pre-operative expenses	1600.00
	iii) Contingencies	500.00
	iv) Interest during construction	1800.00
	Total:	9810.00

SUMMARY OF CAPITAL OUTLAY

		(Rupees in thousands)
1.	Land and land development	2000.00
2.	Main plant and equipment including erection and commissioning	2780.00
3.	Services, offsite facilities and Misc. expenditure	11700.00
4.	Working capital	2073.00
5.	Misc.	215.95
		18768.95

6) **WORKING CAPITAL**

(based on three months requirements)

	(Rupees in thousands)
P_2S_5	378.00
Methanol	198.00
Phenol	870.00
HNO_3	180.00
H_2SO_4	54.00
Cl_2	85.00
Toluene	73.00
Emulsifier	100.00
NaOH	41.00
	2075.00

COST OF PRODUCTION

			(Rupees in thousands)
1.	**Raw Material Cost:-**		
	P_2S_5	21x1000 @ Rs.110/- MT	2310.00
	Methanol	150x1000 @ 4000/- MT	600.00
	HNO_3	180x4000 @ Rs.4000/- MT	720.00
	Phenol	43x8000 @ Rs.8000/- MT	3480.00
	H_2SO_4	36x5000 @ Rs.600/- MT	216.00
	Cl_2	150x700 @ Rs.700/- MT	105.00
	Toluene	70000 x4.30 @ 43000/-KL	300.00
	Emulsifier	20x20000 @ Rs.20000/- MT	400.00
	Nacl	100x1640 @ Rs.1640/- MT	164.00
			8695.00
2.	**Utilities:-**		
	Water	100,000 gallons/ton @ Rs.1/- KL	100.00
	Power	3456x1000KWH @ Rs.85/- per KWH	430.00
	Steam	3000 M³/tonne	30.00
			560.00
3.	**Salaries and Wages:-**		
	Labour (direct) Labour (indirect) and Supervisory staff Overhead 50% of direct labour		798.00
4.	Maintenance @ 5% on plant & Machinery		90.00
5.	Depreciation @ 15% on plant & Machinery		870.00
6.	Interest on total investment (involving equital and sepital cost @ 18%)		3700.00
			5458.00
	1.	8695.00	
	2.	560.00	
	3 to 6	5458.00	
		14713.00	
	Cost of production per ton:		87.50

LIST OF EQUIPMENTS FOR METHYL PARABEN PLANT

	Quantity	Material of construction	Capacity
PCMA UNIT			
1. Reaction kettle	1 No	GL	1000 Ltrs.
2. Reflux condenser	1 "	GL	[illegible] "
3. Toluene batch tank	1 "	MS	600 "
4. Mech batch tank	1 "	MS	500 "
CHLOROSULPHONIC ACID UNIT			
5. Chlorinator	2 "	GL	500 "
6. Reflux condenser	2 "	GL	
7. Storage tank	1 "	RL	7000 "
METHYL PARABEN UNIT			
8. Reaction kettle	1 "	GL	1000 "
9. Reflux condenser	1 "	GL	
10. Toluene recovery vessel	1 "	MS	1000 "
11. Batch tank	1 "	MS	500 "
MISCELLANEOUS EQUIPMENTS			
12. Pumps for pumping and transfer of material from one vessel to another	4 Nos	CI	
13. Storage tank for H_2SO_4, NaOH, toluene, nitric acid, emulsifier phenol, hydrochloric acid, Sod. MS etc.	10 "		7 days storage capacity
PCNB. p-NITROCHLORINE UNIT			
14. Reaction kettle	1 "	GL	1000 Ltrs.
15. Wash tank	1 "	RL	1000 "
16. Batch tank	1 "	MS	500 "
17. Batch tank	1 "	MS	500 "

SPECIFICATIONS OF THE END PRODUCTS

a) **Indian Standard Specifications (IS:2770-1965)**

Acidity (as H_2SO_4)	0.1% (max.)
Active content	98% (min.)
Water	0.1% (max.)
Material insoluble in acetone	0.1% (max.)
Sp. gravity at 25° C	1.317 (min.)

b) **W.H.O. Specifications (WHO/MAL/71.813 i)**

Sr.No.	Requirement	Limits	
		Max.	Min.
1.	O,O-Diethyl O-4 (nitrophenyl) Phosphorothioate content % by weight	90.0	-
2.	Acidity % by weight, calculated as H_2SO_4	-	0.3
3.	Solid matter insoluble in acetone % by weight	-	0.3
4.	Water content, % by weight	-	0.3
5.	Sp. gravity at 25°C/25°C	1.3337	-

BY-PRODUCTS and EFFLUENTS.

1. By-Products.	Quantities
i) Hydrochloric Acid - 30%	105 Tons .
ii) Sodium hydrogen sulphide.	65 Tons .
iii) O-Nitrophenol.	240 Tons .
iv) Sodium chloride.	Not economical to recover.

2. Effluents.

(a) Gaseous Effluent.

Gaseous effluent consist of the following:

(i) Hydrogen sulphide.

This is either recovered by absorbing in sodium hydroxide solution to produce sodium hydrogen sulphide (used extensively in leather tanning industry) or disposed of by burning.

(ii) Chlorine.

Traces of residual chlorine is removed by scrubbing with caustic solution.

(iii) Hydrochloric acid.

Suitable absorption system is required with re-circulation system to produce saleable hydrochloric acid.

(b) Liquid Effluent.

The liquid effluent normally contains dissolved solids mainly NaCl, NaOH and traces of organophosphorous compounds, oils and solvents. Treatment of waste water normally is done by inbuilt facilities in process like hydrolysis with hot alkali, extraction

with solvents etc. followed by implant separators which consist of absorption towers containing regenerable granular active carbon etc. The final water is then collected in a common separator for final separation of solid, oil and solvent. This after bio-oxidation is then discharged out of factory.

Normally down stream water is not recommended for any other use.

Waste Products.

(i) Oils and solids are about 0.25 tons per day and are disposed off by incineration.

(ii) Liquid about 2000 gallons per day.

SAFETY AND ENVIRONMENTAL CONSIDERATIONS

i) The condensation reaction has to be carried out in a closed vessel as the bye-product gases are quite toxic and also a nuisance.

ii) During recovery of solvents at the purification stage incidence of explosions have been reported.

iii) Methyl parathion is highly toxic to warm blooded animal both through inhalation and skin absorption. It is, therefore of utmost importance that due care is taken for workers safety during manufacturing state and also at the time of application.

iv) The process evolves such toxic gaseous effluents like H_2S, nitrousoxide fumes etc. and liquid effluent containing traces of methyl parathion thiophosphoric acid , nitrophenols etc. Due care is required to control exit of these effluents into environment.

v) Due to highly toxic nature of this pesticide, stricter control measures must be adopted in regard to packaging, storage, distribution, application etc.

MAN POWER REQUIREMENT

Sr.No.	Personnel	No.
1.	General Manager	1
2.	Production Manager	1
3.	Engineering Manager	1
4.	Finance Manager	1
5.	Commercial Manager	1
6.	Personnel Manager	1
7.	Security Officer	1
8.	Stores Officer	1
9.	Accountants	2
10.	PA to GM	1
11.	Receptionist	1
12.	Typist clerks	4
13.	Driver	1
14.	Peon	1
15.	Watchmen	6
16.	Shift Supervisor	4
17.	Maintenance Supervisor	3
18.	Plant Operators	8
19.	Skilled workers	4
20.	Unskilled workers	14
21.	Chemists	2
22.	Boiler operator	4
23.	Refrigeration operator	4
24.	Fitter/welder	4
25.	Fitter helper	4
26.	Electrician	2
27.	Electrician helper	2
28.	Instrument mechanic	1

BASIC MANUFACTURERS OF METHYL PARATHION & THEIR ADDRESSES

1. BAYER AG
   SPARTE PFLANZENSCHUTZ ANWENDUNGSTECHNIK
   300, LEVERKUSEN BAYERWERK
   FEDERAL REPUBLIC OF GERMANY

2. CHEMINOVA
   P.O. BOX 9 DK 7620 LEMVIG, DENMARK
   TELEPHONE: (07) 82-41-00

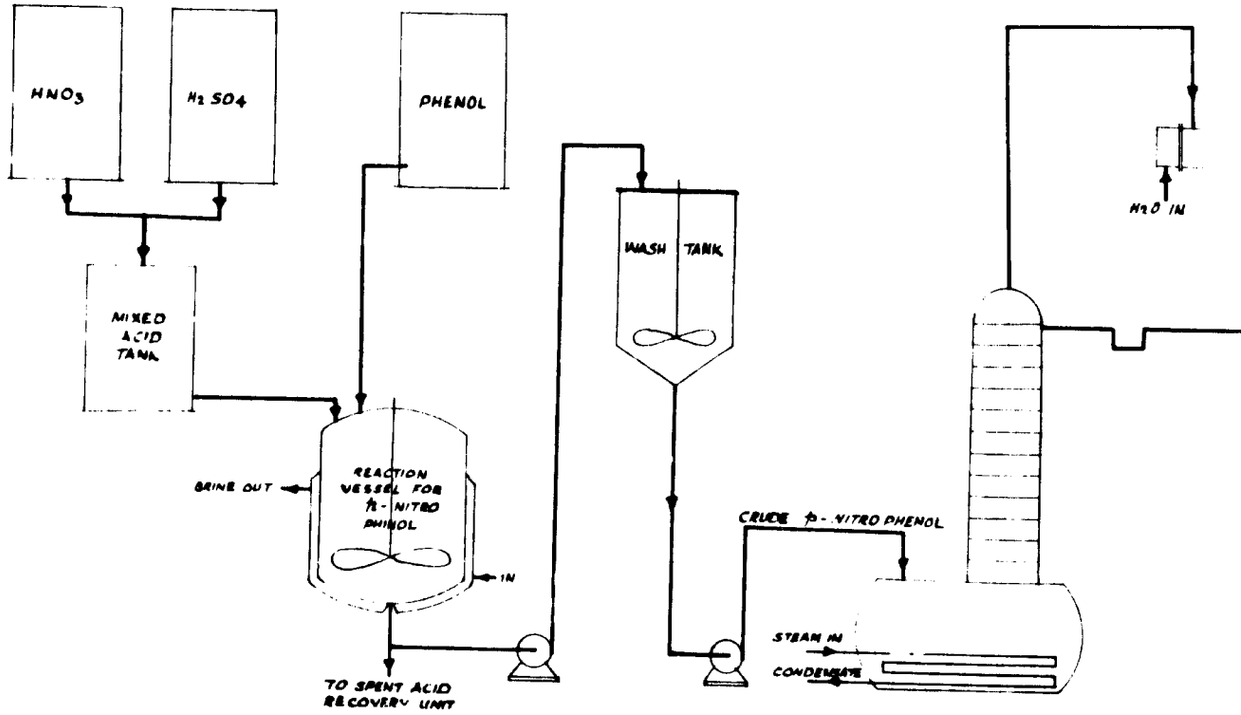
3. KERR-McGEE CHEMICAL CORPORATION
   KERR-McGEE CENTRE
   OKLAHOMA CITY, OKLAHOMA, U.S.A. - 73125
   TELEPHONE: (405) 236-1313

4. MONSANTO AGRICULTURAL PRODUCTS COMPANY
   800 N LINDBERGH
   ST. LOUIS, MISSOURI, U.S.A. - 63166
   TELEPHONE: (314) 694-1000

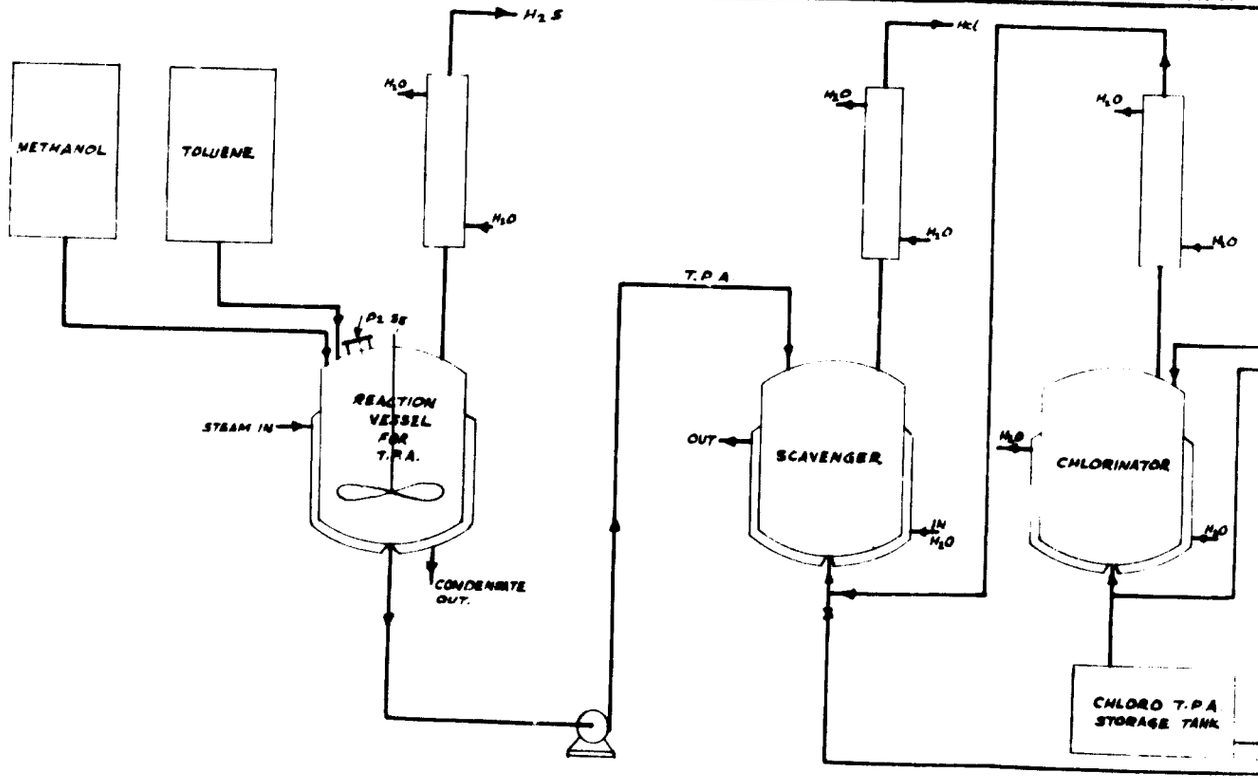
5. STAUFFER CHEMICAL COMPANY
   AGRICULTURAL CHEMICALS DIVISION
   WEST PORT, CONNECTICUT, U.S.A. - 06880
   TELEPHONE: (203) 226-1511

6. BAYER INDIA LIMITED
   EXPRESS TOWERS
   NARIMAN POINT, BOMBAY, INDIA - 400 021

MANUFACTURE OF P-NITRO PHENOL



MANUFACTURE OF METHYL PARATH



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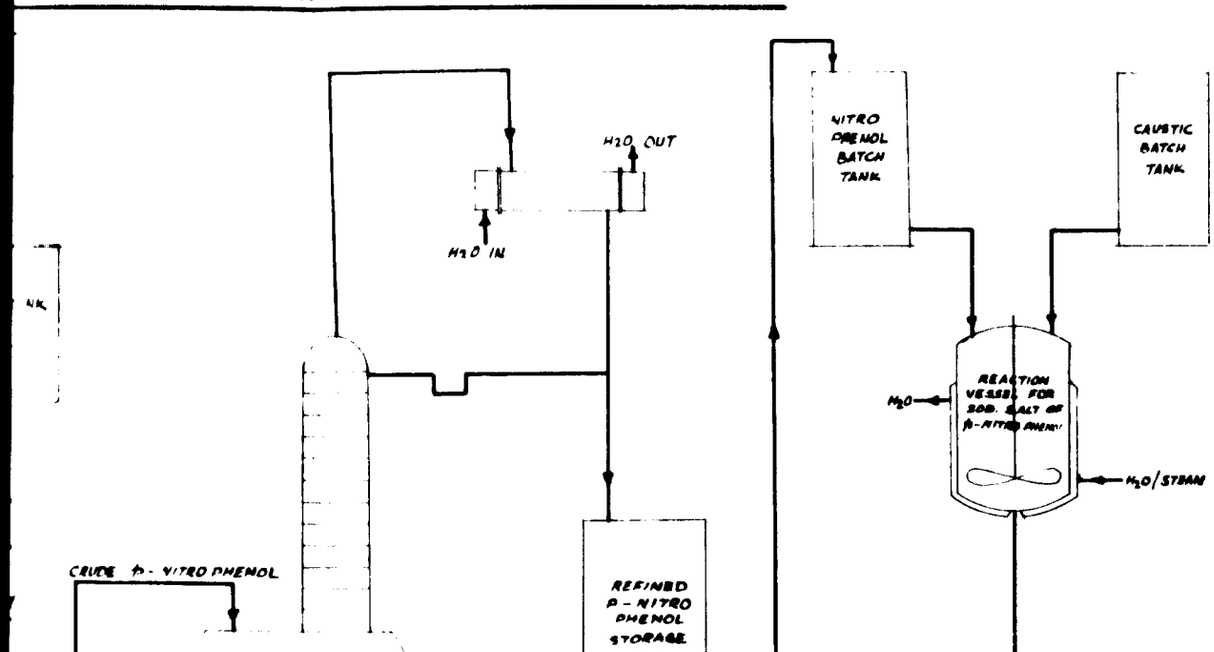
CTURE OF P-NITRO PHENOL SODIUM SALT



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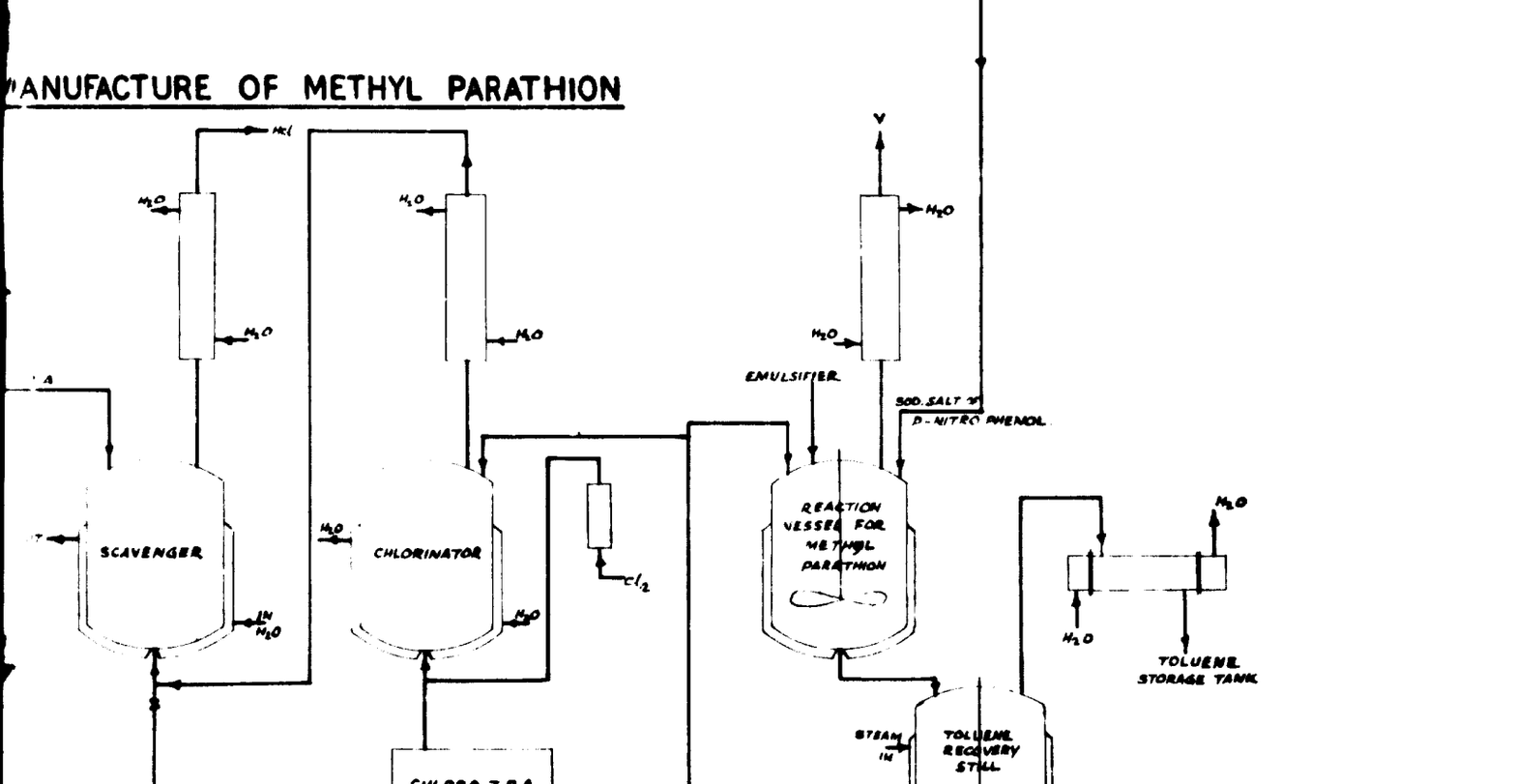

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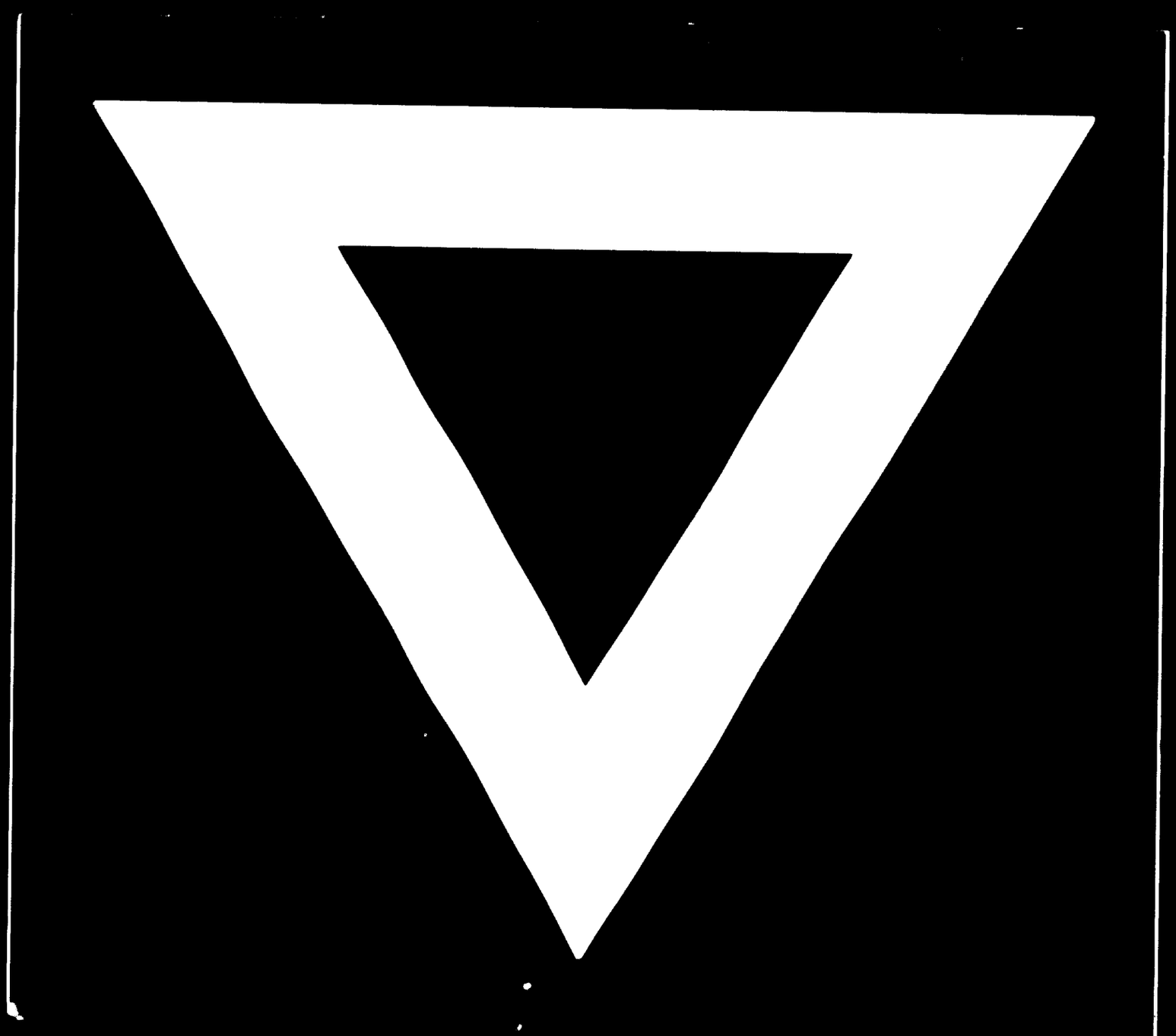

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