OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

FAIR USE POLICY

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

RESTRICTED

17127

DP/ID/SER.A/1078
17 November 1988
ORIGINAL: ENGLISH

ESTABLISHMENT OF A MULTIPURPOSE PESTICIDE PILOT PLANT

DP/EGY/81/006

ARAB REPUBLIC OF EGYPT

Technical report: Findings and recommendations*

Prepared for the Government of the Arab Republic of Egypt
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of R. Gardon, consultant in plant safety

Backstopping officer: B. Sugavanam, Chemical Industries Branch

United Nations Industrial Development Organization
Vienna

3a/l

* This document has not been edited.

V.88 30877

ABSTRACTS

This report has been written after a mission of five days involving visit, discussions about the pesticide pilot plant of KAFR EL DAWAR Chemical and Dyestuff Co, completed by a visit to RHONE POULENC Pesticide Production Plant.

The pilot plant is for the main part well designed except for the glass part which could be in stainless steel and the storage of solvents which should be nitrogen covered.

The employees seem to have the background knowledge to work in safety in such a plant with good information on the risks. Training should be done on each safety procedure at least annually. Medical management is based on a good method but must be more accurately used. Attention should be taken to potential environment problems for the liquids in case of fire and the build up of organic wastes if there is no incineration possibility.

Better care should be taken to the handling (during shipping and in the plant) and to the storage of the raw material especially P_2S_5 and flammable products in drums.

INTRODUCTION :

The following job description gives the duties of the mission :

The consultant in association with the Plant Manager is expected to assess the existing conditions in the pilot plant and make suitable recommendations to follow the safety protocol in a plant manufacturing hazardous chemicals. He will give advice on the protocol to be followed, classification of hazardous areas, modification to be done to improve safety procedure, suggest organization set-up to be followed so that all safety precautions are taken during all shifts. He will also give lectures, if necessary, to all staff of the plant in the area of plant and worker safety and emergency measures.

He will submit a report on his findings and recommendations.

This report gives the recommendations for better safety conditions in this pesticides pilot plan for plant, workers and environment.

Left hand sides of the pages state the existing conditions, right hand sides of the pages give information advice and recommendations.

Some additionnal documents on products handled are attached to the report.

The main parts of the report are :

- organization of the mission
- description of the plant engineering and process
- review of all safety aspects of the plant : engineering, employees, fire, environment, medical, storage.

1 - ORGANIZATION OF THE MISSION

Briefing in Cairo with Mr SABRY and assistant in charge of administration.

PERSONS MET IN KAFR EL DAWAR :

Mr Saïd M. ATTYIA - General Production Manager who organized all the visits, discussions and meetings.

Mr FATHY - Production Engineer of the pesticide pilot plant.

Mr ASHRAF - Chief of safety of the plant.

Mr LOTFY - Chairman of the plant for a conclusion meeting the last day of the mission.

Unfortunately, the pilot plant was operated only during 1.5 days of the 5 days we spent in the plant (impeller of a pump broken).

2 - DESCRIPTION OF THE PILOT PLANT : Engineering, process, products :

2.1 ENGINEERING :

The pilot plant has been built for 350 T/year of **Dimethoate**, to be extended to 500 T/year, and 75 T/year of **Malathion**.

The process for the production of Dimethoate and Malathion is from the Spanish company **ARGONESAS**. The building of the pilot plant was completed in October 1987.

All the informations about the process, the products and the engineering are in two books provided by ARGONESAS.

The safety information is not always given with practical details.	
The pilot plant is built on the side of a production unit of dye stuff; two sides are not closed and the pilot plant is naturally ventilated. There are four levels; all the apparatus is inside the building, except for the solvants storage tanks and the sewage treatment tanks.	O K
All the levels have a minimum of two emergency exits.	O K

2.2 PROCESS :

A : DIMETHOATE : 7 steps.

For reactions see annex n° 1.

1/ Dimethyl dithiophosphoric acid production

By reaction in toluene of sulfur pentasulfide with methanol at a temperature of 55-60°C to 70-80°C at the end of the reaction.

The toluene is dried by azeotropic distillation before feeding the reactants. The reactor is under Nitrogen flow which remove the Hydrogen sulphide produced. Hydrogen sulphide is absorbed in a scrubber with caustic soda. The sodium sulphide produced and used in another unit for dye stuff. The hydrogen sulphide not absorbed is destroyed in an scrubber with sodium hypochlorite.

2/ Sodium salt production :

Sodium hydroxide is added to the solution of acid in toluene at 18°C until pH reaches 7.5.

The sodium salt is decanted in the water phase.

Toluene and interphase are treated with sodium hypochlorite and toluene recycled.

3/ Production of ESTER :

By reaction at 60-65°C of the aqueous phase of sodium salt and methychloroacetic acid ester.
After cooling at 20°C : centrifugation.

Separated ester from aqueous phase + interphase which are treated with sodium hypochloride.

4/ Amidation :

By reaction at 0°C of an aqueous suspension of ester with methylamine. Dimethoate cristallizes.

5/ Filtration :

Three washings of the cake with water gives a final product with 8% of water.

6/ Drying at 35°C under vacuum reduces the water content to 0,2 to 0,3% water.
Dimethoate is stored in P.E. bags in drums of 120 kg.

7/ Sewage treatment :

Sodium hypochlorite is added with mixing to the aqueous phases of the process until chlorine content is stable at 0,5%.
The water phase is sent with the other aqueous wastes of the plant. O K
The first two phases of the process are under the vacuum of the two scrubbers NaOH and NaOCl.
(up to now 100 T have been produced).

B : MALATHION :

1/ Idem DIMETHOATE.

2/ Production of Malathion :

By condensation of the acid and of diethylmaleate at 60-65°C in toluene.
Hydroquinone as antipolymerisation agent,
Trimethylamine as a catalyst.

3/ **Washing** by a solution of 20% sodium chlorine + 20% sodium hydroxyde until pH 7, and decantation of aqueous phase.

4/ **Distillation** under vacuum of the organic phase at t°C $\lesssim$ 70°C gives the malathion.

Up to now 6 batches of malathion made;(bad quality).

The safety data sheet of RHONE POULENC and advices are given in annex for all the products underlined.

3 - ENGINEERING CONTROL OF HAZARD :

No corrosion problems but the process lines of the first phase are in glass and too fragile. Furthermore it's difficult to find standard length of glass pipe of 50 mm in diameter.	Stainless steel grade 316 L (composition : C $\leqslant$ 0,03; Cr = 17; Ni = 13; Mo $\geqslant$ 2,5) can be used for the liquid phase and the gas phase. With this grade, the only risk of corrosion is at the interface between gas and liquid. Liquid pipes need to be emptied at each stop of more than 1 week.
- Scrubbing of Hydrogen sulfide gives good results. One measurement made at the end of the first batch after the start up on the 22nd of september gave less than 0.5 ppm of Hydrogen sulfide released in the atmosphere.	The solution of the sodium Hydroxide is changed every two batches, the same measurement of H2S release needs to be made at the end of the second batch.
- All the electrical equipment is explosion proof.	O K
- Coverage with Nitrogen : fed from the plant or by a set of bottles as a safety.	O K
- The pilot plant is under a permanent wind which gives a good natural ventilation.	O K
- The pilot plant is fairly easy to clean. During my visit it was clean but not operated.	Needs to be kept clean. Specially in the area of Phosphorous pentasulfide loading (dry wiping).

4 - EMPLOYEE SAFETY :

The main condition to meet is to have employees well organized, with a good chemical background and well trained.

4.1 Organization :

The shift is headed by a Chemist who analyses the intermediates products and can take decisions. A foreman organizes the shift. 7 workers : 5 or one step of the production, 2 are able to work on any step of the production.

Each worker write the characteristic data of his reaction step on a special sheet.

- All the workers went to the school of the company for three years.

It should give them a good background to do occurately this kind of job: for the three, I meet it seemed to me it is the case. A one week special training for safety per year is scheduled (by the safety department) it includes reminders on the products, the protection, the procedures.

4.2 Personnel protective equipment :

. Rubber gloves with a good grip - no migration of product or solvant.

. Helmet, goggle (shield), shoes.

. At the end of the shift each worker takes a shower and washes his trousers and jacket.

. Masks :
- each worker wears an escape mask for H_2S.
- He has a 600 C.C filter for phosphorous compound and 600 C.C filter for organic (methylamine)

Filter K ammonia should be used for methylamine

There are two self-contained breathing units with one bottle each, on the second floor, for special use and in case of emergency.

A second set of two is needed on the ground level in case of emergency.

All the employees need to be trained at least twice a year to use the breathing equipment.

4.3 Control of the working conditions :

The concentration of the two toxic gases in the pilot plant needs to be checked and recorded at least once a month. Additional measurements should be done when an apparatus is open.

Nothing is done now.

* Hydrogen sulfide :

The existing Draeger tube allows an accurate measurement at the place where H_2S can be released and at the vent after the Hypochlorite scrubber. Exposure should always be $<$ 10 ppm on a 8h/day basis. When we measured we found 0.5 ppm and there was a leak. Without a leak it should be possible to maintain H_2S concentration at less than 1 ppm everywhere.

* Phosphorus compound :

The Draeger special tube has to be bought. ref. catalog n° 67 28 461.
It does not give exact data in terms of phosphorus compound; it sets the maximum concentration allowed in the plant; it is a biological measurement based on cholinesterase inhibition. These measurements are better than smelling as they provide standards.

4.4 Skin protection :

For any spillage on a worker the clothes must be removed promptly. All the affected areas of the body should be washed thoroughly with soap and water (15 minutes), except the eyes which will be washed only with water.

There is a shower on each level.

They should be painted yellow in order to be seen easily.

5 - FIRE SAFETY :

5.1 Process Equipment :

Reactor RI 101 ((1st reaction) and RI 105 (Toluene distillation) are covered by nitrogen.	OK
All the other vessels containing toluene, methanol, methylamine are only vented to the atmosphere	All The vessels which can have products with flash point < 50°C need to be collected and covered by Nitrogen (around 20 g pressure with a 50 cm water release valve).
The atmosphere of all these vessels is flammable, the risk of having a spark is low, but in the event of a spark, the danger is very high (explosion of a tank).	

5.2 Fire protection equipment :

Powder A B C D E	
11 X 12 kg powder fire extinguishers in the three levels of the pilot plant. 2 X 250 kg powder fire extinguishers near the pilot plant. 4 X 250 kg powder fire extinguishers are in other parts of the plant and can be used within 10 minutes. 1 X 1000 kg powder fire extinguisher on a truck.	The quantities are OK but each Extinguisher need to have a place marked with red paint and must always be at the same place.
Water sprinkler :	
On each level this is opened by a manual valve on a groundfloor.	This valve should be painted red, and a panel should recall its use.

5.3 Equipment repair :

If flamme is required in the pilot plant all the vessels with flammable are emptied and washed, and people from "safety department" smell to find out if there is toluene or methanol.	Smell does not give an accurate information. There are two explosimeters (brand AUER) which need to be used. But they need to be calibrated before each measurement with a standard mixture of flammable product in Nitrogen; can be bought from a company which sells for DRAEGER in Egypt : ARAB COMMERCIAL OFFICE Aly Ibrahim HASSAN 9 (B) Abou L Feda St. P.O Box 134 ZAMALEC CAIRO Tél. 23 41 51 58 71 45 Télex 093473 Before using the flame : - The vessel is cleaned - Flange is put in place in order to isolate all the pipes going to and from the vessel. Fire will be allowed only if the flammable content of the atmosphere is $\leq$ 10% of the lower explosivity limit inside and outside of the vessel and when there is no motion of flammable product outside of the vessel. 2 firemen with powder fire extinguisher will be near by.

5.4 Training of the workers :

The workers of the pilot plant are trained to handle the 12 kg fire extinguisher and to extinguish a fire. They know how to operate the 250 kg fire extinguisher.	At least one training/year "
The firemen are trained to operate all their equipment	They need to know the details of the different levels of the pilot plant. At least one training in the pilot plant/year.

5.5 Knowledge of the flammable products :

Did not seem to be accurate enough.	Refresher sessions was given to a group of personnel : the production engineer, chemist and foreman. - Flash point, autoflammability temperature. - Flammability limits. - Curves : concentration of flammable products versus oxygen content. - The three conditions under which a product can be ignited : concentration of flammable product oxygen concentration energy - Use of this knowledge - the safest way to handle flammable products - operating the production unit with only one of the conditions permanently met : ventilation, coverage of the storage by inerts. - Mechanism of products used to fight fire : * Cooling : water * Priving of oxygen : powders, foams * Stopping fire expansion : Bromofluorides.

6 - ENVIRONMENT WASTE DISPOSAL (SEWAGE)

6.1 Gas release : cf § 3.

6.2 Requirements for the release of water outside of the plant :

The water of the plant is released to the Mediterranean sea through a special duct.
The requirements are :

C O D	60 ppm
B O D	80 ppm
S	1 ppm
OIL and GREASE	10 ppm
SOLIDS	2000 ppm
POISONS	1 ppm
pH	6 to 9

For the water being released into the sea, an additional test on on fish could be done to make sure the water is no toxic to the fish.
Name of the fish we use :
Brachidams Re Rio
They are very sensitive to toxicity of pesticides.

The average flow rate from the plant is around 15000 m^3/day .
The average flow rate of the pilot plant has never been measured and is estimated at 10 m^3/day.

Measurement of all the characteristics of the wastes of the pilot plant must be done to know if improvement of the water treatment is required or if dilution is good enough.

6.3 Treatment of the water phase :

Aqueous phases of the process water from the three levels of the pilot plant and water from the outside part where the water treatment is situated are collected in an agitated vessel.
Sodium Hypochlorite is added to these waters with mixing until % chlorine stays stable at 0.5%.
Water is sent through a small channel then through pipe to the main water treatment of the plant.

- Before sending the treated water to the main water treatment test with the AUER Explosimeter to make sure the liquid sent is not flammable (Toluene, methanol or methylamine....).
If it is flammable because of Toluene decant again the aqueous phase.

If it is flammable because of water soluble flammable products dilute until the vapour phase is not flammable

The water treatment area is (built) partly with anti-acid and partly with other concrete materials. It does not seem to be leak proof.

One should make sure that there is no leak and that water falling on this area can't overflow to the surrounding ground.
One should make sure that there is no risk of leakage or overflowing of the duct used to send the sewage to the main water treatment station.

6.4 Water treatment in case of fire :

In case of fire where large quantities of water are poured onto the polluted area, the polluted water would overflow on the ground and/or into the main sewage treatment with no specific treatment for the pesticides.	A large reservoir of 2000 m^3 minimum should be built to collect the water of the plant in case of emergency. This can be built by digging a hole in the ground; a sheet of polyethylen will make it leak proof. In case of fire the water collected can be recycled to fight fire in order to keep the volume of polluted water as low as possible No polluted water should be released. This device may be used by other production units of the plant.

6.5 Treatment of organics of the process and in case of spillage :

Residual toluene	For all products except ester, amide, dimethoate, malathion and malleate, the treatment used by RHONE POULENC is : 1.Stripping of the solvents and recycling. 2.Treatment by chlorine at 50°C and pH 6-7 (or sodium hypochlorite + hydrogen chloride at pH 6-7). Glass lined vessel required. 3.Filtration of solids including organic wax on saw-dust. 4.If required by Dbo or Dco, filtration on active carbon destruction of organics (including residual toluene): incineration. Destruction of P_2S_5 : no experience of big quantities (over some kg). The only way seems to be : **very slow** addition in the first phase reactor of very small quantities of P_2S_5 in a NaOH, NaOCl mixture. Experience has to be gained in controlling carefully H2S pressure, N2 flow, temperature in the water phase. Put some toluene to control the temperature. We have only the experience of one or two kilos : pouring of very large amounts of water on P_2S_5 on a windy day !!.

6.6 Washing of drums : Drums of row materials are re-used to store interme-diates or other materials; but they are not easily and well cleaned before re-use.	A flushing device drowing in annex can be used.

7 - MEDICAL MANAGEMENT and FIRSTAID DISCUSSION WITH Dr N.H.EL ASSI

7.1 Phosphorus compounds :

Seric cholinesterase level measurements are done by the Bohringer method which measure "Erythrocytaire" cholinesterase. Workers should be between 1900 and 3800. If they are under or above this range they don't work in the pesticide plant for one month.
But only two or three measurements have been done since the start up (November 87) and no measurements were done before the first exposures.

Advice of the doctor of ELBEUF plant who use the same method of measurement :

- a measurement should always be done before exposure.

- the individual initial level is the base of interpretation of the following measurements.

- Initial measurements - 30% must be considered as the result of an exposure and the worker removed.

- Higher levels than 3800 make no problem, the worker can work again in pesticide plant.

- In the case of exposure (initial level - 30%), measure after one month. If level at half way between initial level and 1900 can work again in pesticide plant. Total recovery is after 3 months.

- Explanation on the case we discussed of increase of 30% between first and second measurement : the worker has been in contact with organophosphorous before the first measurement; although he worked in the plant between the two measurements he had no further contact with the product.

- In your case (with people who have been exposed) measurement should be done every month to check evolution of individual levels, correlate lowering of more than 30% with exposure. Frequency could be 2, 3 or 4 months if no lowering but always check cholinesterase level in case of liquid spillage on a person.
- The more serious risks of exposure are : handling solid (dimethoate) and skin contact with the product especially with gloves which are not kept clean.
- Solvants, P_2S_5, Flu, cold don't give important variations on "Erythrocytaire cholinesterase level.
- Price of this type of measurement in France : around 120 FF.

7.2 Solvent :

We did not discuss this subject in detail but no specific measurements are done.

For toluene, red haemoglobine level must be checked twice a year.

7.3 Medicines - first aid :

In the medical department workers can get medicine for professional or personal use if they need.

OK
For organophosphorous compound Contrathion (pralidoxime) should be used first (no side effects). This is sold by **SPECIA 16, Rue Clisson 75013 PARIS.**

If no recovery signes use ATROPINE.

7.4 Hydrogen sulphide :
Two workers vanished some months ago.
It is supposed that they breathed Hydrogen sulphide when opening the reactor of the first step. Using filters inefficient (concentration in $H_2S > 2\%$ or filter saturated).

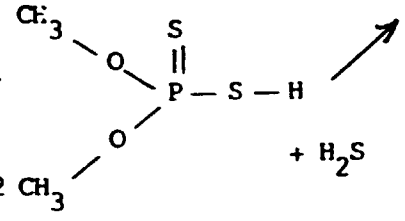
First aid for a person exposed H_2S
1 : remove rapidly from the contaminated area.
2 : provide oxygen (see Chemical Safety data sheet of **Phosphorous Pentasulfide**).

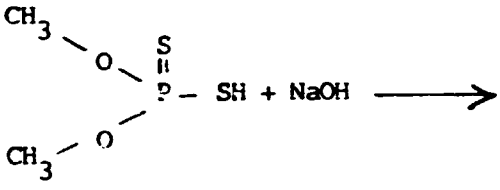
9 - STORAGE OF MATERIALS

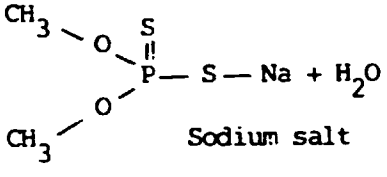
Raw materials : They are stored in three different places.	
1.- Well ventilated hangar : Monomethylamine is stored here with nitrobenzene. Somes drums are palettized; they are in very good shape. Others have been left on their sides, and these have many big bumps. There were cigarettes ends noticed in this storage area.	O K - The drums should be stored on palettes, but direct sun should never shine on the drums. Clear notices should say that fire and smoking are forbidden in this area.
2.- A closed store in which there are : P_2S_5, methylchloroacetate, monomethylamine, hydroquinone, acetanilide, cleve acid, luriant acid. This store is clean.	Monomethylamine should be removed from this store and put in the first store (well ventilated). In this store, there are flammable products and the lights are not flamme proof. Apparently electricity is not used. Remove it.
3.- Another closed store in which there are : P_2S_5 - some drums are in very bas shape and enclosed in a polyethylene bag. Diethylmalleate - most of the drums are old and dirty.	 O K General problem for drums : drums which do not contain oxydising products should be stored on palettes. It is more stable to have several layers. We saw many drums with big bumps, some of them were open or almost open. That might be dangerous for the whole storehouse. Transportation company must be warned of this.

REACTIONS

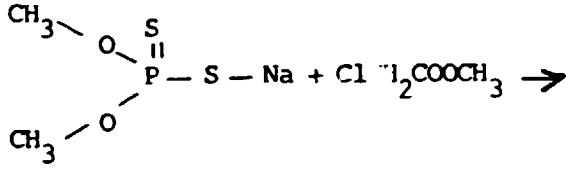
A - DIMETHOATE

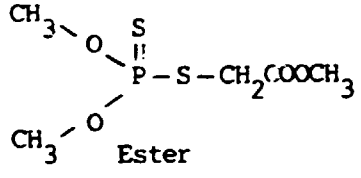
1)- $P_2S_5 + 4\ CH_3OH \longrightarrow$  $+ H_2S$

2)- 

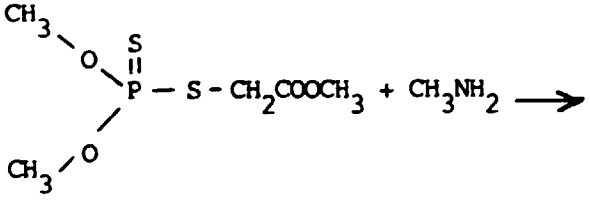


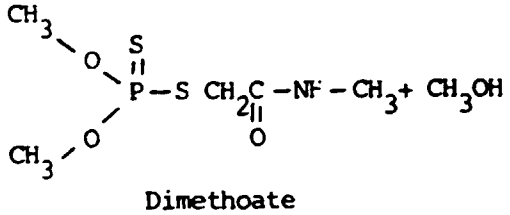
Sodium salt

3)- 



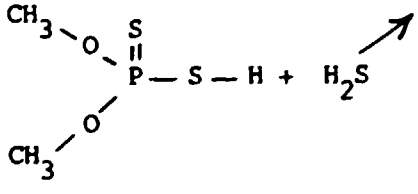
Ester

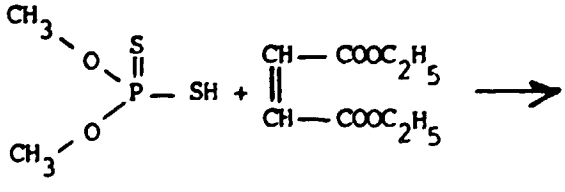
4)- 

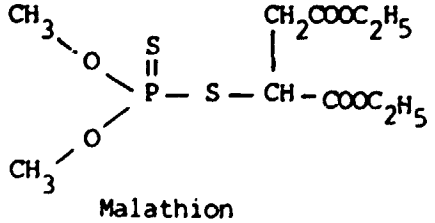


Dimethoate

B - MALATHION

1)- $P_2S_5 + 4CH_3OH \longrightarrow 2$  $+ H_2S$

2)- 



Malathion