

Topic 13

HAZARDOUS CHEMICALS :
Physical & Environment

Hazardous Chemical (Definition)

Any substance having properties that can cause permanent or temporary injury to individual in contact with the chemicals



CHEMICAL THAT CAN CAUSE PHYSICAL HAZARD

CHEMICAL HAS A PHYSICAL HAZARD WHEN THERE IS SCIENTIFICALLY VALID EVIDENCE THAT IT IS ANY OF THE FOLLOWING:

- **ASPHYXIANT**
- **FLAMMABLE**
- **EXPLOSIVE**
- **PHYROPORIC** – spontaneously burns when expose to air
- **WATER REACTIVE**
- **COMPRESSED GAS**
- **CRYOGENIC**

ASPHYXIANTS

➔ CHEMICALS THAT DEPRIVE BODY TISSUES OF OXYGEN

There are two types of Asphyxiants Chemicals:

1. **Simple asphyxiants** ➔ act by diluting or displacing atmospheric oxygen, which lowers the concentration of oxygen in the air
 - **Breathing air with low oxygen** can result in insufficient oxygen in blood and tissues, causing headache, unconsciousness and eventually death
 - **Inert gases** such as **helium and argon** are example of simple asphyxiants
 - Simple asphyxiants, when present in high concentrations in air act by **limiting the availability of oxygen**, without producing significant physiological effects on the body
 - Simple asphyxiants usually do **not have threshold limit values** (TLVs)
 - The **minimum oxygen content** of air should be 18% by volume under normal atmospheric pressure

Examples of Simple Asphyxiants

Asphyxiants	CAS No.	Chemical Formula	Description
Acetylene	74-86-2	C ₂ H ₂	Colorless gas with a faint odor Commercial grade has a garlic like odor
Argon	7440-37-1	Ar	Inert, monoatomic gas, colorless, odorless, tasteless
Carbon dioxide	124-38-9	CO ₂	Colorless, odorless gas
Ethane	74-84-0	C ₂ H ₆	Colorless, odorless gas
Ethylene	74-85-1	C ₂ H ₄	Colorless gas with a sweet odor and taste
Helium	7440-59-7	He	Inert, monoatomic gas, colorless, odorless, tasteless
Hydrogen	1333-74-0	H ₂	Diatomic gas
Methane	74-82-8	CH ₄	Colorless, odorless, tasteless gas
Natural gas			Lighter than air, warning odor system available
Neon	7440-01-9	Ne	Inert, monoatomic gas, colorless, odorless, tasteless
Nitrogen	7727-37-9	N ₂	Diatomic gas, colorless, odorless, tasteless

2. Chemical Asphyxiants

Acts in two way:



Prevent uptake of oxygen in the blood - example CO

- Inhibits normal oxygen transfer either from the blood to the tissues or within a cell - example HCN, H₂S

Asphyxiants	CAS No.	Chemical formula	TLV-TWA
Aniline (phenylamine, aminobenzene)	62-53-3	C ₆ H ₅ NH ₂	2ppm 7.6mgm ⁻³
Carbon disulfide	75-15-0	CS ₂	10 31
Carbon monoxide	630-08-0	CO	25 29
Cyanogen (dicyan)	460-19-5	C ₂ N ₂	10 21
Hydrogen cyanide	74-90-8	HCN	4.7 5
Hydrogen sulfide	7783-06-4	H ₂ S	10 14
Nitrobenzene	98-95-3	C ₆ H ₅ NO ₂	1 5
Toluidene	95-53-4	CH ₃ C ₆ H ₄ NH ₂	2 8.8

TLV (Threshold Limit Value) - of a chemical substance is a level to which it is believed a worker can be exposed day after day for a working lifetime without adverse health effects

TWA (Time Weighted Average) – The average concentration under which most people can work consistently for eight hours

FLAMMABLE COMPOUNDS

- **Most common in chemical laboratory**
- **Ability to vaporize, ignite and burn or to explode varies with specific type or class of substance**
- **Prevention of fires and explosions requires knowledge of flammability characteristics**
 - **Ignition temperature**
 - **Flash point**
 - **Limit of flammability**

IGNITION TEMPERATURE

- **Minimum temperature required** to initiate or cause self-sustained combustion independent of the heat source
- It differs from the flash point in that a flame, spark, or other ignition source is not required to start the fire

Example: diethyl ether (ignition temperature 160°C) can be ignited by the surface of hot plate

Glowing light bulb may ignite carbon disulfide (ignition temperature 80°C)

FLASH POINT

- The **flash point is the lowest temperature, as determined by standard test**, at which a liquid gives off vapor in sufficient concentration to form an ignitable mixture with air near the surface of the liquid within the test vessel. The concentration required is the lower explosive limit (LEL)
- **Example: An open beaker of diethyl ether set on the laboratory bench next to a Bunsen burner will ignite, where as a similar beaker of acetic acid will not**
 - Diethyl ether : F.P -45°C
 - Acetic acid : F.P 42.8°C
- **Many common laboratory solvents and chemicals have flash points that are lower than room temperature**

LIMITS OF FLAMMABILITY

- * It is possible for a **flammable liquid** to be **above its flash point** and yet **not ignite in the presence** of an adequate **energy source**. The explanation for this phenomenon lies in the composition of a fuel-air mixture that maybe too lean or too rich for combustion
- * Each **flammable gas or liquid** (as a vapor) has two fairly limits defining the range of concentrations in **mixtures with air that will propagate flame and explode**

LEL – lower explosive limit

UEL– upper explosive limit

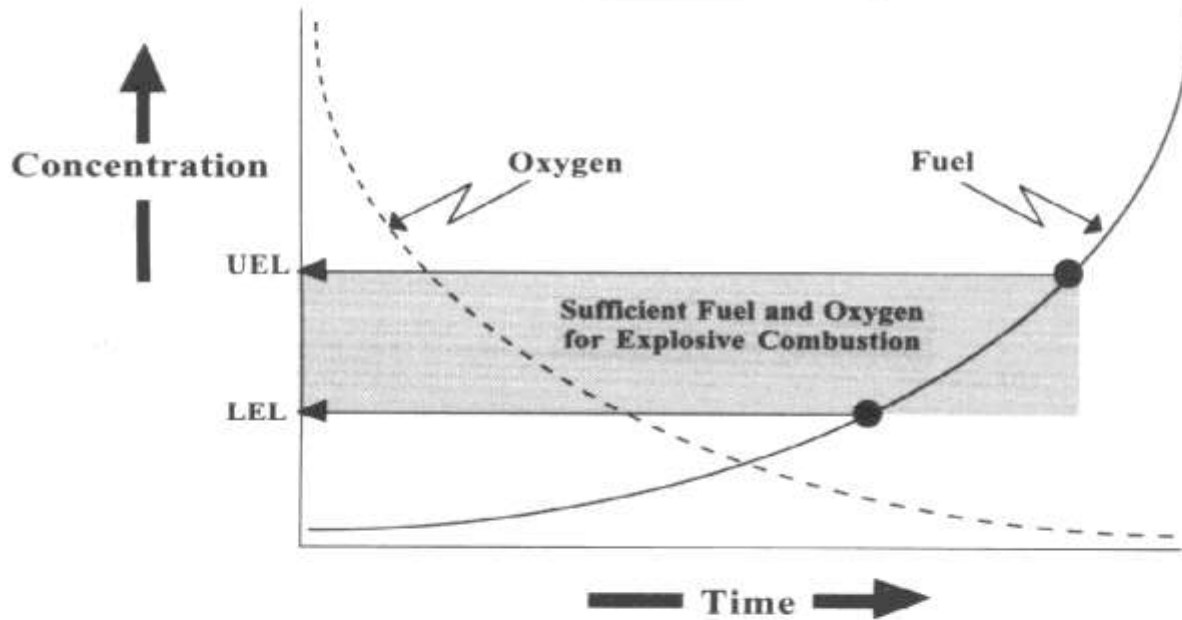
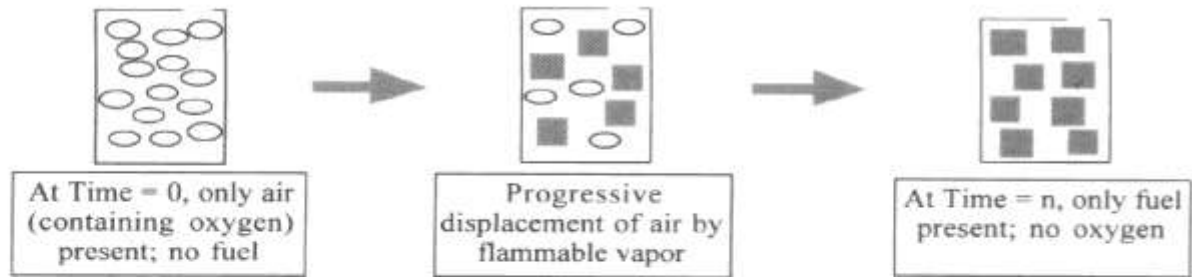


FIGURE 16.1 Lower and upper explosive limits. As the air in a container is progressively displaced by a flammable vapor (upper portion of figure), the concentration of oxygen in the container decreases while the concentration of potential fuel increases. At concentrations of fuel (expressed as percentage of atmosphere) below the LEL (lower explosive limit), there is too little fuel to support burning; at concentrations of fuel above the UEL (upper explosive limit), there is too little oxygen to support burning. Explosion may occur only when the relative concentrations of fuel and oxygen are at or between the LEL and UEL. On a scale where 100% represents the LEL, 10% is typically used as the trigger for implementing personnel evacuation.

Hazardous Properties of Some Common Laboratory Chemicals

Chemical	Class	Flash Point (°C)	Boiling Point (°C)	Ignition Temp. (°C)	Flammable Limit (% by volume in air)		Vapor Density	U.L Flammability Rating
					Lower	Upper		
Acetaldehyde	1A	-37.8	21.1	175.0	4.0	60.0		
Acetic acid		42.8			5.4			
Acetone	1B	-17.8	56.7	465.0	2.6	12.8	2.0	
Amyl acetate		25.		399.	1.1		4.49	90
Benzene	1B	-11.1	80.0	560.0	1.3	7.1	2.77	55-60
Butyl alcohol		100.		371.	1.4		2.55	95-100
Carbon disulfide	1B	-30.0	46.1	80.0	1.3	50.0	2.64	40
Carbon tetrachloride		None		None	None		5.32	110
Cyclohexane	1B	-20.0	81.7	245.0	1.3	8.0	2.9	0
Ethyl acetate		-4.		427	2.2		3.04	
Ethyl alcohol	1B	12.8	78.3	365.0	3.3	19.0	1.59	High
Ethyl ether		-45.		180.	1.9		2.56	70
Ethylene dichloride		-7.		429.	6.2		3.4	100
n-Heptane	1B	-3.9	98.3	215.0	1.05	6.7		
n-Hexane	1B	-21.7	68.9	225.0	1.1	7.5		
Isopropyl alcohol	1B	11.7	82.8	398.9	2.0	12.0		
Methane (gas)		-7.		Low	5.0		0.55	High
Methyl alcohol	1B	11.1	64.9	385.0	6.7	36.0	1.11	70
Methylene chloride		None					5.37	
Methyl ethyl ketone	1B	-6.1	80.0	515.6	1.8	10.0		
Pentane	1A	-40.0	36.1	260.0	1.5	7.8		
Petroleum ether		-56.		246.	1.4		2.5	95-100
Styrene	1B	32.2	146.1	490.0	1.1	6.1		
Tetrachloroethane		None		None	None			0
Toluene	1B	4.4	110.6	480.0	1.2	7.1	3.14	75-80
p-xylene	1C	27.2	138.3	530.0	1.1	7.0		

CLASSES OF FLAMMABLE AND COMBUSTIBLE LIQUIDS

CLASS	BOILING POINT	FLASH POINT	EXAMPLES
	°C (°F)	°C (°F)	
Flammable 1A	< 37.8 (100)	< 22.8 (73)	Ethyl ether, pentane
Flammable 1B	≥ 37.8 (100)	< 22.8 (73)	Acetone, ethyl alcohol
Flammable 1C	< 37.8 (100)	≥ 22.8 (73)	Butanol, isoamyl acetate
Combustible 2	-	37.8 (100) ≤ and < 60 (140)	Formalin, cyclohexanone
Combustible 3A	-	60 (140) ≤ and < 93.3 (200)	Phenol, dichlorobenzene
Combustible 3B	-	≥ 93.3 (200)	Ethylene glycol, mineral oil

Source: National Fire Protection Association, 1987. *Flammable and Combustible Liquids Code, NFPA 30*

BASIC RULE FOR USING FLAMMABLE SUBSTANCES

1. **Flammable substance** should be handled only in **areas free of ignition sources**.
2. **Flammable substance** should **never be heated by using an open flame**. Preferred heat source include **steam baths, water baths, heating mantles, and hot air baths**.
3. When **transferring flammable** liquids in metal equipment, **static – generated sparks** should be avoided by bonding and the use of ground straps.
4. **Ventilation is one of the effective ways** to prevents the formation of flammable mixtures. An exhaust hood should be used whenever appreciable quantities of flammable substances are transferred from one container to another, allowed to stand in open containers, heated in any other way.

EXPLOSIVES CHEMICALS

- Any chemical that causes an almost immediate pressure, when subjected to sudden shock, pressure or heat
- In general, **compounds containing** the following **functional group** tend to be **sensitive to heat and shock**:

Acetylide, azide, diazo, halamine, nitroso, ozonide and peroxide

Example: a. **CH₂N₂ (diazo methane)**

Explode explosively when compressed

b. **Sodium azide** is used in **vehicle air bags** to inflate them quickly

c. **Diethyl ether, isopropyl ether, dioxane**

form dangerous peroxides upon aging in glass in the presence of air

OTHER EXAMPLES OF CHEMICALS WHICH ARE EXTREMELY SHOCK SENSITIVE

- a. Acetyl nitrate – formed when **nitric acid** is combined with **acetic anhydride**.
- b. Ammoniacal silver nitrate ($\text{AgNO}_3 + \text{NH}_4\text{OH}$) solutions, when allowed to stand, **formed silver fulminate, a shock sensitive explosive**.
- c. Perchloric acid (60 – 70% aqueous HClO_4). **Perchloric acid** in contact with easily **oxidizable organic** material is **sensitive to heat and impact**.
- d. **Ammonia (NH_3)** reacts with **iodine to give NH_4I** which is explosive and with hypochlorites to give chlorine.
- e. **Dry benzoyl peroxide ($\text{C}_6\text{H}_5\text{CO}_2$)** is easily ignited and sensitive to shock.
- f. **Chlorine (Cl_2)** react violently with **hydrogen (H_2)** or with hydrocarbon when exposed to sunlight.

Guidelines when dealing with shock sensitive and explosive chemicals

- Write the **date received** and **dates opened** on all containers of shock sensitive chemicals. Some chemicals become increasingly shock sensitive with age.

E.g. Perchloric acid

- Ethers which contain peroxide should not be distilled
- Unless the manufacturer added an inhibitor, closed containers of shock sensitive materials should be discarded after 1 year
- **Wear appropriate personal protective equipment** when handling shock sensitive chemicals

PYROPHORIC

- **Pyrophoric** chemicals are chemicals that **ignite spontaneously in air**.
- **Pyrophoric** chemicals can **react explosively** when they come into **contact with air**.
- The most common **pyrophoric** chemicals include **phosphorus, alkylated metals, metal alkoxides and halides**.
- Pyrophoric chemicals must be stored in tightly closed containers under an inert atmosphere (or, for some, an inert liquid), and all transfers and manipulations of them must be carried out under an inert atmosphere or liquid.

WATER REACTIVE

Water reactive chemicals can develop pressure; generate flammable, explosive, corrosive or toxic gases; or ignite or explode when exposed to water or moisture.

Alkali and alkaline-earth metals (sodium, lithium, calcium, potassium, magnesium)

Aluminium chloride

Anhydrous metal halides (aluminium tribromide, germanium tetrachloride)

Anhydrous metal oxides (calcium oxide)

Benzoyl chloride

Calcium carbide

Calcium oxide

Nonmetal halides (boron tribromide, phosphorous pentachloride)

Nonmetal halide oxides (inorganic acid halides, phosphoryl chloride, sulfuryl chloride, chlorosulfonic acid)

Nonmetal oxides (acid anhydrides, trioxide)

COMPRESSED GAS

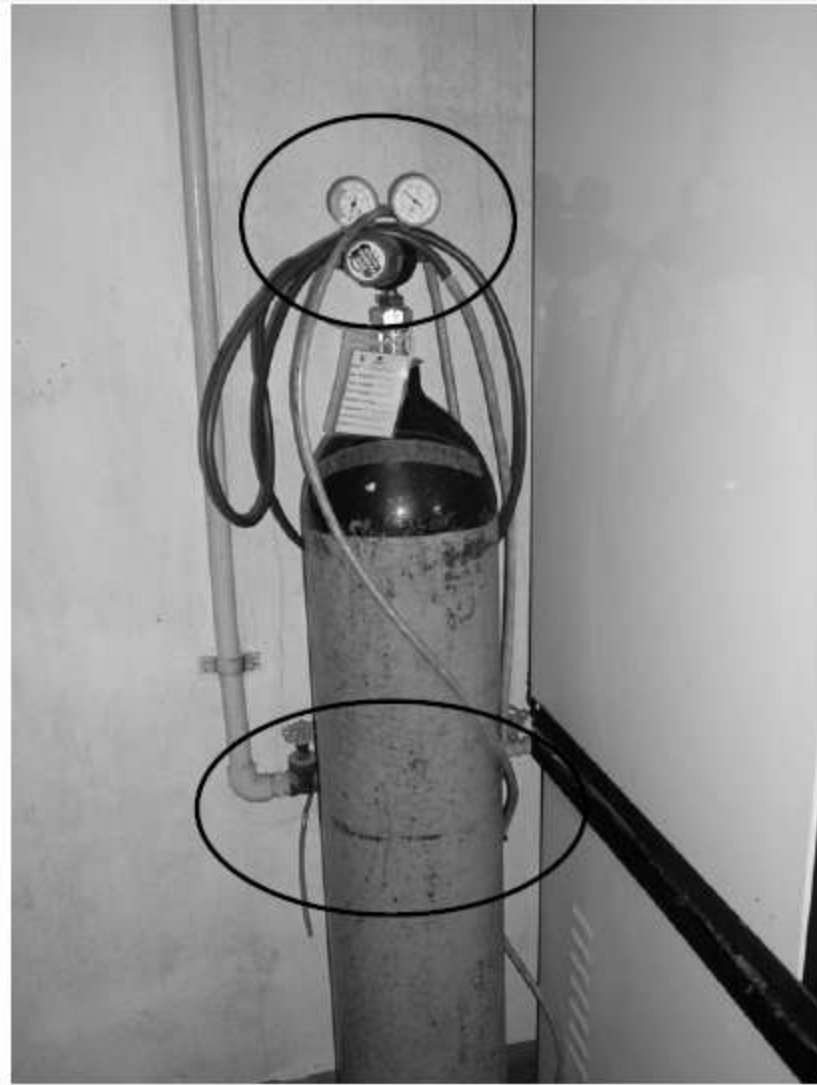
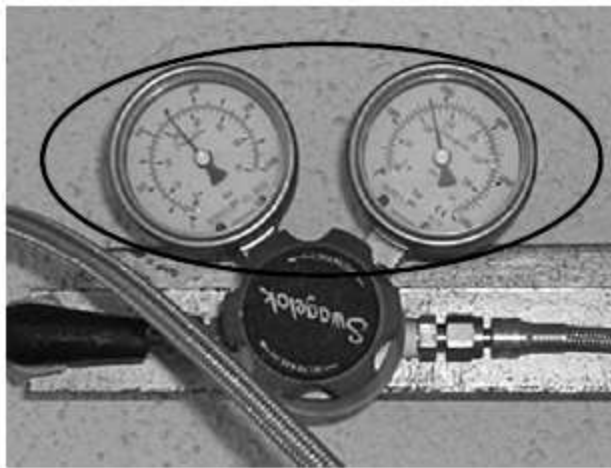
Definition: any materials or mixtures in containers having an absolute pressure in excess of 40psi at 20°C or in excess of 194psi at 55°C

Considered as high energy sources - treated as potential explosives

Cylinder Storage

- **Store in special storage area**
 - * **Store oxygen away from flammable gases**
 - * **The valve protection cap must be kept on all the times, except when the cylinder is in use**
 - * **Chain must be chained or strapped, or otherwise mounted, in place to prevent them from falling over**
 - * **Corrosive gases should be stored for the shortest possible time period, under 3 month**

Spot the error?



Chain Correctly ?



A good example !



Safety procedure for Handling of Compressed Gas

- Only **trained staff** may handle compressed gases
- Know the **gas cylinder content**. Understand the properties and hazards of gas before using it. Refer to MSDS.
- A fire hose and other **fire fighting equipment** should be easily **available**.
- Where necessary, a **self-contained breathing apparatus** should be available in the vicinity of the working area.

Safety procedure for Handling of Compressed Gas (cont....)

- **Fasten cylinders securely** in the upright position whether in use or storage. Cylinders should not be allowed to drop nor be struck violently.
- **Handle** cylinders **carefully** and transport them on a wheel cart. Never roll, drag or throw gas cylinders.
- **Caps used for valve protection** should be kept on the cylinders at all times except when the cylinder is actually being used.
- Never temper with the valve and close cylinder valve when not in use.

Safety procedure for Handling of Compressed Gas (cont....)

- **Oxygen cylinders** (empty or fill) in storage should be **separated from fuel-gas cylinders** and combustible materials.
- **Full and empty** cylinders of all gases should be stored **separately**.
- The concentration of **toxic or flammable gas** in the atmosphere of the store should be **periodically monitored**. An explosimeter (combustible gas monitored. indicator or manual gas detection tubes with hand pump) may be used.
- **Do not use** gas cylinders without the **proper regulator**.

Safety procedure for Handling of Compressed Gas (cont....)

- Always **check the regulator** before attaching it to the cylinder. If the connections do not fit together readily, the wrong regulator is being used.
- **Do not permit oil or grease** to come in contact with cylinders or their valves.
- **Attach the regulator securely** before opening the valve wide. Always use a cylinder wrench to tighten the regulator nut and hose connections.
- **Do not repair cylinder valves or regulators by yourself**

CORROSIVE

- Chemical that cause damage and destroy tissues or organ when exposed
- Acid – HCl , HF , HNO_3 , H_2SO_4
- Alkali – NaOH , KOH , CaO
- Gas – Cl_2 , NO_2 , SO_2
- Halides – BCl_3 , PCl_3 , SiCl_4 , AlCl_3 – direct addition of these substances to water produce a violent reaction

Handling Corrosives

- **Wear suitable PPE** –natural rubber glove, goggle, lab cloth, etc
- **Add concentrated acids or caustic powder/solids to water** with constant stirring and cooling, never the reverse
- **Never mix conc. Acids with caustic**
- **Never mix caustics with chlorinated solvents**

CRYOGENIC SYSTEM

- Cryogenic is a science of very low temperature i.e. $< -73^{\circ}\text{C}$
- Low temperatures obtained by liquidification or solidification of gases

Gas	Normal Boiling Point ($^{\circ}\text{C}$)	Volume Expansion to Gas	Flammability	Toxicity	Odor
Carbon dioxide	-78.5	553:1	No	Yes	Slightly pungent
Hydrogen	-252.7	861:1	Yes	No	No
Nitrogen	-195.8	696.1:1	No	No	No
Helium	-269.0	3757:1	No	No	No
Argon	-185.7	847:1	No	No	No
Fluorine	-187.0	888:1	No	Yes	Sharp
Oxygen	-183.0	860:1	No	No	No
Methane	-161.4	578:1	Yes	No	No

CRYOGENIC SYSTEM - *Hazard and Handling*

Hazard - extreme coldness  frostbite and tissues damage

- Accumulated vapors may acts as asphyxiates
- Increase fire hazard through condensation of atmospheric oxygen when liquefied inert gas in contact with cold metal
- Affect properties of other materials - rubber/ metal alloys may become brittle and disintegrate

- Handling:**
1. Use special container
 2. Avoid confined areas where vaporization occurs
 3. Ensure that all apparatus is properly vented to prevent accumulation of pressure
 4. Always wear chemical splash goggles
 5. Wear long sleeves and/or a lab coat
 6. Do not wear watch, ring that can trap the material
 7. Use glove (heavy duty?)

CHEMICALS THAT ARE HAZARDOUS TO ENVIRONMENT

- Persistence in the environment
- The following criteria are recommended to define a substance as persistent:

$t_{1/2} > 30$ days in air

$t_{1/2} > 50$ days in soil, sediment, water, sludge or any other media

Example:

* **Heavy Metal**

* **Aromatic Hydrocarbon**

* **Pop (Persistent Organic Pollutant)** e.g. Polychlorinated Biphenyl (PCB), Dichloro Diphenyl Trichloro Ethane (DDT)