

## CHAPTER 7

## RIOT CONTROL AGENTS

## SECTION I - GENERAL

**701. Introduction.**

Riot control agents are irritants characterised by a very low toxicity (chronic or acute) and a short duration of action. Little or no latent period occurs after exposure. Orthochlorobenzylidene malononitrile (CS) is the most commonly used irritant for riot control purposes. Chloracetophenone (CN) is also used in some countries for this purpose in spite of its higher toxicity. A newer agent is dibenzoxazepine (CR) with which there is little experience. Arsenical smokes (sternutators) have in the past been used on the battlefield. Apart from their lachrymatory action they also provoke other effects, e.g., bronchoconstriction and emesis and are some times referred to as vomiting agents. For historical reasons some older, more toxic compounds are briefly mentioned.

## SECTION II - LACHRYMATORS

**702. CS (Orthochlorobenzylidene Malononitrile).**

CS is used as a riot control agent in many countries. It is also commonly used as a training agent for simulation of chemical warfare conditions and for testing of respirators. The limit of perception by taste ranges from 0.25-0.5 mg.m<sup>-3</sup>. The minimal irritant concentration ranges from 0.1- 1.0 mg.m<sup>-3</sup>, the IC<sub>50</sub> from 5-10 mg.m<sup>-3</sup>, and the LC<sub>50</sub> for persons very much larger, estimated as 60,000 mg.min.m<sup>-3</sup>. This provides a high margin of safety in its use.

**703. Properties.**

CS is the code name for orthochlorobenzylidene malononitrile. On account of its stronger irritant effects and its lower toxicity it has superseded CN. It is a white crystalline solid substance. Volubility is very poor in water, moderate in alcohol and good in acetone, chloroform, methylene dichloride, ethylacetate and benzene. CS is unstable in aqueous solution. If enough CS can be dissolved in water (e.g., by adding propylene glycol or other organic co-solvent) spraying fluids with an irritant action of short duration result. Although the smoke is non-persistent, CS may stick to rough surfaces (e.g., clothes) from which it is released only slowly. At least 1 hour of aeration is necessary to cleanse such materials from CS after exposure. CS is usually dispersed as an aerosol generated pyrotechnically, or by spraying a solution of CS in a suitable solvent.

**704. Detection.**

The CS cloud is white at the point of release and for several seconds after release. Exposure is associated with a pepper-like odour, the presence of intense eye effects, dyspnoea, coughing and rhinorrhoea.

**705. Protection.**

Full individual protective equipment will provide complete protection. Protection against field concentrations of irritant agents is provided by the respirator and ordinary field clothing secured at the neck, wrists and ankles. Individuals who handle CS should wear rubber gloves, hood, rubber boots, rubber apron and respirator and secure their field clothing at the neck, wrists and ankles.

**706. Decontamination.**

- a. Exposed persons should if possible move to fresh air, separate from fellow sufferers, face into the wind with eyes open and breathe deeply.
- b. Following exposure, clothing and individual equipment should be inspected for residue. If a residue is found, individuals should change and wash their clothing to protect themselves and other unmasked persons.

**707. Mechanism of Action.**

- a. Lachrymators act on the nerve endings, the cornea, mucous membranes and the skin. The reaction is very rapid.
- b. The toxicity of CS is very low, the estimated lethal concentration over 1 hour for people being  $1000 \text{ mg.m}^{-3}$ , whereas a concentration of  $1 \text{ mg.m}^{-3}$  is intolerable to most people.

**708. Pathology.**

Pathological examination of rabbits exposed to CS revealed an increase in number of goblet cells in the respiratory tract. Pulmonary oedema occurred after inhalation at very high concentrations, in excess of  $20000 \text{ mg.min.m}^{-3}$ . Experiments in dogs showed that the animals dying as a result of exposure to very high concentrations died from obstruction of the upper respiratory tract; inhalation of CS through an intratracheal cannula, on the other hand, caused pulmonary oedema.

**709. Signs and Symptoms.**

During exposure an individual is incapable of effective concerted action.

**710. CS Exposure Symptoms.**

Exposure to CS causes the following symptoms:

- a. *Eyes.* Symptoms include a violent burning sensation, conjunctivitis (lasting up to 30 minutes), erythema of the eyelids (lasting about an hour) blepharospasm, violent lachrymation (over 10-15 minutes) and photophobia.
- b. *Respiratory Tract.* The first symptom is a burning sensation in the throat, developing into pain and extending to the trachea and bronchi. At a later stage a sensation of

suffocation may occur, often accompanied by fear. In addition a burning sensation in the nose, rhinorrhoea, erythema of the nasal mucous membranes and sometimes mild epistaxis occurs. The sense of taste is often distorted for some hours after exposure. Nausea, diarrhoea and headache have been observed. Sneezing occurs after mild exposure and may be persistent. Many exposed people have reported fatigue for some hours afterwards. Coughing, choking, retching and (rarely) vomiting occur after exposure.

- c. *Skin.* A burning sensation occurs especially in moist areas, but soon disappears. This burning sensation may recur some hours later, often while washing the area. Prolonged exposure to large amounts (e.g., when handling CS in bulk) can cause erythema and vesicle formation. Prolonged exposure, continuous or intermittent, to high concentrations, combined with high temperatures and humidity in the field may result in a cumulative effect. Sensitivity to CS may be provoked. It has been shown that the particle size affects the clinical result. Small particles (1-5  $\mu\text{m}$ ) affect the eyes and respiratory tract more rapidly than larger ones (20-30  $\mu\text{m}$ ) but recovery after exposure to small particles is more rapid. Very large particles (50  $\mu\text{m}$ ) affect the eyes more than the respiratory tract, while recovery is slower.

### 711. First Aid.

- a. In practically all cases it is sufficient to take the patient into fresh air where the symptoms will soon disappear. Clothing should be changed. If symptoms persist the eyes, mouth and skin may be washed with water (and with soap in the case of the skin). Oil based lotions should *not* be used. Skin decontaminants containing bleach should *not* be used, but should be reserved for more dangerous contamination (e.g., vesicants or nerve agents); bleach reacts with CS to form a combination which is more irritant to the skin than CS alone. Chest discomfort can usually be relieved by reassurance.
- b. CS hydrolyses more rapidly in alkaline solutions and an acceptable skin decontamination solution is 6.7% sodium bicarbonate, 3.3% sodium carbonate and 0.1% benzalkonium chloride.

### 712. Therapy.

- a. *Eyes.* Ordinarily the eye effects are self limiting and require no treatment. If large particles or droplets of agent have entered the eye, treatment as for corrosive materials may be required. Prompt irrigation with copious amounts of water is the best treatment for solid CS in the eye. After complete decontamination corticosteroid eye preparations may be used. Patients who have been heavily exposed must be observed for possible development of corneal opacity and iritis.
- b. *Skin.* Early erythema and stinging sensation (up to 1 hour), especially in warm moist skin areas, are usually transient and require no treatment. Inflammation and blistering similar to sunburn may occur after heavy or prolonged exposure, especially in fair skin. Acute contact dermatitis should be managed initially in the same way as any other acute dermatitis. Corticosteroid cream or calamine lotion

may be applied to treat existing dermatitis or to limit delayed erythema. Oozing may be treated with wet dressings of 1 in 40 aluminium acetate solution for 30 minutes three times daily. A topical steroid should follow the wet dressing immediately. Secondary infection is treated with appropriate antibiotics. Significant pruritus can be treated with calamine lotion or corticosteroid preparations. If blisters develop these should be treated as any other second degree burn.

- c. *Respiratory Tract.* In the rare event of pulmonary effects from massive exposure, evacuation is required. Management is the same as that for lung damaging agents (Chapter 4).

### 713. Course and Prognosis.

Most personnel affected by riot control agents require no medical attention and casualties are rare.

### 714. CR (Dibenzoxazepine).

- a. CR is similar in its effects to CS, but the minimum effective concentration is lower and the  $LCt_{50}$  is higher. Symptomatology and treatment are similar to those of CS.
- b. It is a pale yellow crystalline solid which melts at 163°F (73°C) and is stable in organic solutions. It has limited volatility in water and is not hydrolysed in aqueous solutions. It has a pepper-like odour. The agent is currently used only in solution for dissemination in liquid dispensers. The solution in the dispensers contains 0.1% CR in 80 parts propylene glycol and 20 parts water. In organic solutions, CR is an eye irritant at concentrations down to 0.0025% or even lower. CR differs from CS in being less toxic when inhaled but CR skin effects are more pronounced. It is more persistent in the environment and on clothing.

### 715. CN (Chloracetophenone).

CN is a riot control agent and as a training agent is now superseded by CS, the latter being much less toxic. However, it is still in use by police in some countries.

### 716. Properties.

CN is a clear yellowish brown solid, with a melting point of 54 °C. It is poorly soluble in water, but dissolves in organic solvents. The white smoke smells like apple blossom. The minimal irritant concentration is 0.3 mg.m<sup>-3</sup>. It has been estimated from experimental data that the  $LCt_{50}$  for people is 7000 to 14000 mg.min.m<sup>-3</sup>, but inhalation of 350 mg.m<sup>-3</sup> for 5 minutes may be dangerous. The  $ICt_{50}$  is 20 to 40 mg.min.m<sup>-3</sup>. CN is more toxic than CS.

### 717. Mode of Action and Toxic Effects.

The mode of action is similar to that of CS; CN causes stimulation of sensory nerve endings.

**718. Signs and Symptoms.**

Exposure to CN primarily affects the eyes, producing a burning sensation, lachrymation, inflammation and oedema of the eyelids, blepharospasm, photophobia and, at high concentrations, temporary blindness. The severest of these symptoms is reached in a few minutes and then gradually decreases. After about 1 or 2 hours all symptoms disappear. High concentrations can cause irritation of the upper respiratory tract, inflammation of the skin with vesicle formation, visual impairment and pulmonary oedema. Drops or splashes in the eye may cause corrosive burns, corneal opacity and even permanent visual impairment. Drops or splashes on the skin may cause papulovesicular dermatitis and superficial skin burns. Ingestion of food or water contaminated with CN causes nausea, vomiting and diarrhoea.

**719. First Aid.**

After limited operational exposure ill effects will be adequately neutralised by letting fresh air blow into the open eyes. If necessary the eyes maybe washed with water from the water bottle (canteen). The eyes should never be rubbed as mechanical injury may complicate the chemical effect. Patients suffering from temporary blindness should be reassured; permanent blindness from exposure to *vapour* has never been observed even at very high concentrations.

**720. CA (Bromobenzyl Cyanide) and BA (Bromoacetone).**

Bromobenzyl cyanide (CA) and bromoacetone (BA) are older lachrymators. They are too toxic for use as riot control agents and must be considered obsolete. Their properties are listed in Table 7-I.

*Table 7-I. Properties of CA and BA*

Property	CA	BA
Appearance	Yellow, solid	Colourless liquid
Melting point	25°C	-54°C
Boiling point	227-242°C	136°C
Specific gravity	1.52	1.63
Solubility in water	Poor	Poor
Solubility in organic solvents	Good	Good
Volatility (mg.m <sup>-3</sup> )	130 (30°C)	75000 (30°C)
Smoke vapour odour	Rotting fruit	Stinging
Smoke vapour colour	White	Colourless
Minimal irritant concentration	0.3 mg.m <sup>-3</sup>	1.0 mg.m <sup>-3</sup>

## SECTION III - VOMITING AGENTS

**721. Introduction.**

Vomiting agents produce strong pepper-like irritation in the upper respiratory tract with irritation of the eyes and lachrymation. They cause violent uncontrollable sneezing, cough, nausea, vomiting and a general feeling of bodily discomfort. The principal agents in this group are diphenylchlorarsine (DA), diphenylaminearsine chloride (Adamsite (DM)) and diphenylcyanarsine (DC). DA, DM, and DC are also classed as sternutators. They are dispersed as aerosols and produce their effects by inhalation or by direct action on the eyes.

**722. Properties.**

- a. *Characteristics.* They are non-persistent agents. The particles fall to the ground after dispersion and are virtually ineffective unless resuspended. Di-phenyl-cyanoarsine (DC) is the most irritating of the group. The principal characteristics of these agents are summarised in Table 7-II.
- b. *Visual Detection.* It should be remembered that the colour of the solid agent depends on the degree of purity (technically raw products are often coloured) but the colour and odour of the smoke after dispersion may no longer be noticeable in concentrations which are nevertheless still highly irritant, so that odour and colour cannot be relied upon for detection.
- c. *Toxicity.* The following data are applicable to DM. The  $LCt_{50}$  estimated for people is 13000 to 44000  $mg \cdot min \cdot m^{-3}$  depending on the means of dissemination of the agent. The  $ICt_{50}$  for man ranges from 22 to 150  $mg \cdot min \cdot m^{-3}$ . The maximum concentration which is stated to cause no permanent damage after inhalation for 5 minutes is 100  $mg \cdot m^{-3}$ .

*Table 7-II. Properties of Vomiting Agents*

Property	DM	DA	DC
Appearance	Yellow or green solid	Colourless, crystalline	Colourless, solid
Melting point	195°C	38°C	38°C
Boiling point	410°C	330°C	346-337°C
Specific gravity	1.68	1.4	
Solubility in water	Poor	Poor	Poor
Solubility in organic solvents	Poor	Good	Good
Volatility ( $mg \cdot m^{-3}$ )	0.02 (20°C)	0.68 (20°C)	1.5 (20°C)
Smoke vapour odour	Coal fire	Shoe polish	Garlic
Smoke vapour colour	Yellow	White or grey	White
Minimal irritant concentration	0.1 $mg \cdot m^{-3}$	0.1 $mg \cdot m^{-3}$	0.25 $mg \cdot m^{-3}$

**723. Detection.**

The use of these agents may be suspected by the clinical symptoms and signs.

**724. Protection.**

Full individual protective equipment will provide complete protection. The standard protective respirator and ordinary field clothing gives adequate protection against field concentrations of vomiting agents.

**725. Mechanism of Action.**

This consists of inhibition of the SH containing enzymes, especially those of the pyruvate dehydrogenase system. These enzymes play a part in the energy producing processes in the cell. The integrity of the cell structure depends on the proper functioning of the metabolic processes and inhibition of the enzyme mentioned interferes with cell respiration resulting in the destruction of cell structure.

**726. Pathology.**

Vomiting agents produce local inflammation of the upper respiratory tract, the nasal accessory sinuses and the eyes.

**727. Signs and Symptoms.**

- a. The onset of symptoms may be delayed for several minutes after initial exposure (especially with DM); effective exposure may, therefore, occur before the presence of the smoke is suspected. If the mask is put on then, symptoms will increase for several minutes despite adequate protection. As a consequence, the casualties may believe their mask is ineffective and by removing it expose themselves further.
- b. Inhalation is followed by a burning sensation in the nose and throat, hypersalivation, rhinorrhea, coughing, sneezing, nausea and vomiting. Mental depression may occur during the progression of symptoms. The paranasal sinuses are irritated and fill with secretions and severe frontal headache results. Prolonged exposure may cause retrosternal pain, dyspnoea and asthma-like symptoms. Symptoms reach their climax after 5 to 10 minutes and disappear 1 to 2 hours after cessation of exposure. Effects on the eyes are slight and are restricted to a burning sensation and lachrymation. Exposure of the skin to high concentrations will cause erythema and itching, proceeding to a burning sensation and vesicle formation. On the battlefield, high concentrations are not likely to occur so that affection of the eyes and skin is unlikely. Ingestion of food and water contaminated by sternutators may cause nausea, vomiting, diarrhoea (sometimes bloodstained) and weakness and dizziness have been reported.

- c. High concentrations are not expected in the open owing to movement of air, but may be met within enclosed spaces (shelters, tents, etc.), and under these circumstances the skin may show vesicle formation, capillary damage and localised swelling, while corneal necrosis and pulmonary oedema are possible results. Unsteady gait and a positive Romberg sign have been reported. Other neurological results of severe exposure include hyperaesthesia, anesthesia and paraesthesiae, especially in the legs. Loss of consciousness has been reported.

#### **728. Treatment.**

- a. Put on the protective mask and wear it in spite of coughing, sneezing, salivation and nausea. Lift the mask from the face briefly if necessary to permit vomiting or to drain saliva from the facepiece. Carry on with duties as vigorously as possible - this will help to lessen and shorten the symptoms. Combat duties usually can be performed despite the effects of vomiting agents.
- b. In spite of the dramatic appearance of the syndrome, the only treatment necessary is first aid. The patient should not smoke for some hours. If necessary the mouth may be rinsed with water, but the water should not be swallowed. The eyes and skin may be washed with water. Clothing should be well brushed. In cases of severe exposure treatment as for lung damaging agent poisoning may be required. A mild analgesic may be given to relieve headache and general discomfort.

#### **729. Course and Prognosis.**

Symptoms of exposure to field concentration of vomiting agents usually disappear in 20 minutes to 2 hours, leaving no residual injury. However, a few instances of severe pulmonary injury and death have occurred due to accidental exposure to high concentrations in confined spaces.