Department of the Environment
Industry Profile

Chemical works

explosives, propellants and pyrotechnics manufacturing works

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Contaminated Land and
Liabilities Division

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The purpose of these publications is to provide regulators, developers and other interested parties with authoritative and researched advice on how best to identify, assess and tackle the problems associated with land contamination. The publications cannot address the specific circumstances of each site, since every site is unique. Anyone using the information in a publication must, therefore, make appropriate and specific assessments of any particular site or group of sites. Neither the Department or the contractor it employs can accept liabilities resulting from the use or interpretation of the contents of the publications.

The Department's Contaminated Land Research Report series deals with information needed to assess risks; procedures for categorising and assessing risks; and evaluation and selection of remedial measures.

General guidance on assessing contaminated land and developing remedial solutions which is complementary to the Department's publications is provided by the Construction Industry Research and Information Association (CIRIA).

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DOE Industry Profile

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Preface

DOE Industry Profiles provide developers, local authorities and anyone else interested in contaminated land, with information on the processes, materials and wastes associated with individual industries. They are not definitive studies but they introduce some of the technical considerations that need to be borne in mind at the start of an investigation for possible contamination.

Every site is unique. Investigation of a site should begin with documentary research to establish past uses. Information on the site's history helps to focus a more detailed investigation. This knowledge needs to be supplemented by information on the type of contamination that may be present and where on site it may be found. Profiles give information on the contamination which might be associated with specific industries, factors that affect the likely presence of contamination, the effect of mobility of contaminants and guidance on potential contaminants.

The date when industrial practices first commenced on a site and its location are important clues in establishing the types of operations that may have taken place, so each profile provides a summary of the history of the industry and its likely geographical spread within the United Kingdom.

Profiles should be read with the following reservations in mind:

> individual sites will not necessarily have all of the characteristics described in the profile of that industry;
>
> practices can vary between sites and change over time;
>
> as practices change, problems of possible contamination may also change;
>
> the profile may refer to practices which are no longer followed, and may omit current practices which avoid contamination.

The risks presented by contaminated sites depend on the nature of the contaminants, the targets to which they are a potential threat (such as humans or groundwater) and the routes or pathways by which they reach these targets. The current or proposed use of a site and its environmental setting are crucial in deciding whether treatment is necessary and if so, the methods to be used. Some sites may not need treatment.

The information in profiles may help in carrying out Control of Substances Hazardous to Health (COSHH) assessments for work on contaminated land - see Health and Safety Guidance Note HS(G) 66 *Protection of workers and the general public during the development of contaminated land,* Health and Safety Executive, 1991, and *A guide to safe working practices for contaminated sites,* Construction Industry Research and Information Association, 1995.

Note: the chemical names given to substances in this profile are often not the modern chemical nomenclature, but the names used historically for those substances.

Chemical works: explosives, propellants and pyrotechnics manufacturing works

1. Background

1.1 Introduction to explosives

Explosive materials are chemicals or mixtures of chemicals which, when suitably initiated, decompose with the rapid formation of large volumes of hot gases. These gases can cause extremely high pressure if the explosive is set off in a confined space. An explosive material may be a solid, liquid or gelatinous substance.

Methods of initiation include mechanical stimuli (eg impact or friction), the action of heat (eg sparks or an open flame), a detonating shock (eg a blasting cap) and electrical or microwave stimuli. Chemical decomposition reactions include smouldering, deflagration and detonation. The ease with which chemical decomposition can be initiated is known as the 'initiation sensitivity'.

Explosives are commonly categorised as primary (or initiatory) explosives, secondary (main charge or high) explosives, propellants and pyrotechnics. The classification of explosives used in this profile is summarised in Table 1.

Primary explosives are the most sensitive of the above groups and will generally trigger explosive reactions in neighbouring, less sensitive, main charge explosives.

Secondary, or high, explosives are designed to burn supersonically, producing a high velocity shock wave and large volumes of gas. They are manufactured both for military and commercial uses. Military explosives are used in a wide range of equipment including shells, bombs and missiles. Commercial explosives are essential to industries such as mining and quarrying, construction and demolition, and geophysical exploration.

Propellants are generally more sensitive than secondary explosives. They burn at a rapid but regular rate producing a large volume of gas. The rapid rise in pressure of the combustion gases is used to accelerate a bullet or shell along the bore of a gun or to provide thrust to propel a rocket or similar missile. Specialised uses for propellants include starter mechanisms for aircraft engines, aircraft ejector seats and release units held on aircraft.

Pyrotechnic compositions have a wide range of applications including signalling and illuminating flares, fireworks, incendiary devices, smoke flares, explosive igniters and also as propellants.

Matches consist of a head which ignites by friction and a tinder substance to pick up and transmit the flame.

Table 1 Classification of materials referred to in this profile

Explosives	Primary (iniating) explosives	Silver azide Lead azide Lead styphnate Tetrazene
	Secondary (main charge or high) explosives	Military: TNT RDX HMX Tetryl PETN Nitroguanidine NG Picric acid
		Commercial: Ammonium nitrate-based slurries Emulsions and gelatinous explosives NG-based dynamites and gelignites EGDN
Propellants	Solid propellants	NC Single base propellant Double base propellant Triple base propellant Composite propellant
	Liquid propellants	Mono-propellant Bi-propellant Hybrid propellant
Pyrotechnics		Illuminants Smoke compositions Incendiary compositions Delay compositions Priming compositions

Notes:

TNT	2,4,6-Trinitrotoluene
RDX	Cyclotrimethylene trinitramine
HMS	Cyclotetramethylene tetranitramine
Tetryl	Trinitrophenylmethylnitramine
PETN	Pentaerythritol tetranitrate
Picric acid	2,4,6-trinitrophenol
NG	Nitroglycerine
NC	Nitrocellulose
EGDN	Nitroglycerol

1.2 History

The history of explosives manufacture dates back to the 7th Century with the use of gunpowder by the Chinese. Gunpowder was first used in England in the Middle Ages but its use developed slowly until the 16th Century, when powder mills and associated engineering works were established, mostly in the South-East of England. From about that time, arms were manufactured by many small independent producers. The components they produced were not interchangeable and supply in times of war was haphazard. The Royal Gunpowder Factory was established at Waltham Abbey in Essex in the 1780s.

By the beginning of the 19th Century the government began to take over some of the existing ordnance works. During the First World War, the government sought to standardise weapons manufacture and supply by building three large engineering sites. As the demand for a greater variety and more accurate weaponry increased, a number of new ordnance sites were built, to re-stock weapons, update old forms of equipment and research new defence armaments.

The 19th Century also saw the first commercial uses of explosives products, beginning with matches in 1827, subsequently patented in Britain in 1855. Further developments within the industry followed with the production of nitroglycerine (NG) and then nitrocellulose (NC) in the mid to late 19th Century. Commercial production of NG, primarily as 'dynamite', was pioneered by Nobel's Explosive Company (NEC) in the 1860s. The preparation of TNT and Tetryl (see notes to Table 1) followed. Single and double base propellants and picric acid were developed in the late 19th and early 20th Centuries. The years 1935–1945 saw the development of RDX, HMX, plastic explosives (eg mixtures of RDX and plasticisers), various gun propellant formulations (eg 'neonites') and flashless (nitroguanidine) propellants. Many new compositions were developed during and after the Second World War and found applications for commercial as well as military use. During the 1940s and 1950s the commercial use of 'dynamite' was gradually replaced by the use of ammonium nitrate-based explosives. The 1960s saw a shift towards slurry and emulsion explosives and the subsequent development of on-site bulk handling and mixing.

At the end of the Second World War there were 44 Royal Ordnance Factories in operation and several NEC agency factories. It is estimated that about 30 sites were involved in large-scale manufacture of explosives, together with perhaps 50–60 smaller-scale facilities.

In addition to these major facilities there were about 2000 small licensed premises including filling sites and sites for storing or manufacturing small amounts of explosives. Over the past decade, however, the military explosives manufacturing industry has declined and a significant number of production plants have now closed.

1.3 Location

The distribution of explosives handling sites across the United Kingdom has been fairly widespread. The main influences on location are remoteness from centres of population (a legal requirement) and close proximity to railways and major trunk roads, including transport links with key markets; eg naval ports (such as in Scotland and on the South Coast of England), defence facilities etc. Other key markets are the mining and quarrying industries which are concentrated in hard rock areas in Scotland and Northern England. Military pyrotechnics are manufactured in the United Kingdom at many sites, most of which were originally firework factories.

2. Activities

2.1 Raw materials

A variety of raw materials can be used in explosives manufacture. Some may be required in bulk (eg mineral acids, organic solvents, polymers etc) and some in small quantities contained in drums and bags (eg sensitisers, stabilisers, ballistic modifiers, surfactants, raw materials for primary explosives manufacture etc).

2.1.1 Primary explosives

In the formulation of primary explosives, small quantities of the explosive (eg lead azide) in powder form are mixed with minor additives including graphite and surfactants.

2.1.2 Secondary explosives

In the manufacture of military high explosives, the main reagents are mineral acids (nitric and sulphuric acids), organic solvents (such as acetone) and organic compounds such as hexamine for RDX and HMX manufacture and toluene (or mononitrotoluene) for TNT manufacture. Nitric acid is usually produced on site from the catalytic oxidation of ammonia, whilst sulphuric acid is generally bought in. Both acids may be recycled on site after initial use.

The most important raw material in the manufacture of commercial secondary explosives is ammonium nitrate, which is combined with fuels, eg liquid hydrocarbons, and cellulosic materials. Minor additives (eg sensitisers, additional fuels and oxidisers, thickening agents etc) include aluminium powder, sodium nitrate, sodium perchlorate and guar gum. Surplus military explosives may be used as sensitisers, eg TNT or 'Composition B' (a mixture of RDX, TNT and wax).

2.1.3 Propellants

Nitrocellulose (NC) is the basic raw material for single base propellant manufacture and NC/NG 'paste' is the basic raw material for double base propellant manufacture. NC and NG are produced by the addition of mineral acids to cellulose or glycerine respectively. The basic ingredients for triple base propellants are NC/NG 'paste' and a flash suppressant (usually nitroguanidine). Other minor ingredients include potassium sulphate, ethyl centralite (diethyl diphenyl urea), diphenylamine, graphite and dinitrotoluene.

Raw materials in the manufacture of composite propellants include oxidants, such as ammonium perchlorate, and fuels, such as polybutadiene and polyisobutylene.

2.1.4 Pyrotechnics

The main raw materials of pyrotechnics are fuels and oxidants. The main ingredients include charcoal, sulphur, antimony sulphide, metal powders (eg magnesium, aluminium), non-metals (eg boron, phosphorus) and organic materials (lactose and nitrated materials). The most important oxidants include nitrates, chlorates and perchlorates, usually of the alkaline metals and alkaline earth metals.

On ignition, the mixture of fuel and oxidant gives rise to a highly exothermic reaction. Illuminating effects are enhanced by the addition of the metallic powders, coloured effects by metallic salts, and smoke production by inclusion of the phosphorus. Minor ingredients added for either safety reasons or to produce special effects include waxes and organic polymers, barium salts, organic dyes and inert materials such as silica.

2.1.5 Matches

Matches consist of veneer quality poplar treated with paraffin and flame-proofed with ammonium phosphate. The non-safety head contains potassium chlorate and tetraphosphorus trisulphide bound together with glue. White phosphorus was used prior to the 1930s. The safety head contains potassium chlorate and sulphur bound together with glue. The matchbox comprises red phosphorus, ground glass and glue.

2.2 Delivery and on-site storage of raw materials

Historically, the majority of raw materials were delivered by canal and rail. These methods have now been superseded by road vehicle or bulk tanker transport, depending on the type of material and quantities used.

Solid raw materials are generally delivered in quantities ranging from kilograms in bottles to hundreds of kilograms in drums. A range of approved packaging is used for the transport of explosive materials, eg NC is usually transported in water- or alcohol-wet plastic bags contained within sealed drums. Pure NG is rarely transported outside the factory but may be transported mixed with a desensitiser.

Bulk solids, such as baled cellulose and those contained in drums and bags, are generally transferred from the delivery area to their respective storage areas on pallets using fork-lift trucks. Bags and small drums may be manually lifted by process workers. Explosive materials must be stored within secure magazines suitably licensed by the HM Inspector of Explosives.

On-site transfer is usually by fork-lift truck or by narrow-gauge railway.

Bulk liquids (eg acids and organic solvents) are transferred from tankers to storage vessels using a permanent pipe network which is characteristically overhead, although some underground pipework may exist. These liquids are transferred using pump systems to process or storage areas.

2.3 Production processes

2.3.1 Explosives

Primary explosives

Primary explosives are produced in the form of powders with good flow transfer and pressing characteristics to permit high speed automatic loading of detonators and percussion caps. Manufacture is usually a batch process in which metals or metal salts are mixed with mineral acid and/or organic and organometallic solutions to form a precipitate. This often takes place in the presence of a growth modifier in order to produce a material of the required crystal form. The product is generally mixed with binders and other materials which alter the sensitivity of the explosive or modify the effect of detonation. Manufacturing operations are generally conducted by remote control within stainless steel vessels. Batch sizes range from 0.5 kg to 5.0 kg.

The most widely used primary explosives include silver and lead azide, lead styphnate and tetrazene. Mercury fulminate was important historically but has not been used in the United Kingdom since the Second World War.

Secondary explosives (military)
Production of military grade secondary explosives involves the nitration of solid or liquid organic compounds (eg hexamine, toluene, glycerine) by either a batch process (typically 100 kg per batch) or by a continuous process (throughputs typically around 500 kg per hour). Generally, the nitrating acid is mixed with the organic material in a nitration vessel. The reaction is exothermic, with the temperature being controlled by direct cooling and regulation of chemical addition. Multi-stage nitration is used in the manufacture of TNT. Once nitration is complete, the product may be washed with water to remove any residual acid. The crude product is recovered by settlement followed by filtration; it may then be purified by re-crystallisation from an organic solvent such as acetone or cyclohexanone.

TNT manufacture also includes an additional washing step using aqueous sodium sulphite solution to remove non-symmetrical isomers. Dinitrotoluene may be a by-product of TNT manufacture.

HMX is manufactured from hexamine, usually by a batch nitration process involving acetic anhydride, acetic acid and ammonium nitrate. Nitroguanidine manufacture involves the preparation of guanidine nitrate from dicyanodiamide and ammonium nitrate.

The more sensitive high explosives such as RDX are usually mixed with waxes or other explosives to act as desensitisers and binders. The most common mixtures are RDX/wax and RDX/TNT. These mixing operations are batch processes. RDX can be mixed with a plasticiser such as a lithium-based grease to form plastic explosives.

Historically, the manufacture of Tetryl involved mono- and dimethylaniline being dissolved in concentrated sulphuric acid and then poured into concentrated nitric acid. Tetryl was used mainly during the Second World War and has not been manufactured in the United Kingdom in recent decades. Picric acid, which was used as a filling in grenades and mines during the First World War, was prepared by the nitration of phenol dissolved in sulphuric acid. Phenol might therefore be found in picric acid or in plant areas where ammonium picrate was manufactured. Picric acid is extremely toxic and tends to form impact-sensitive salts in contact with certain metals.

Secondary explosives (commercial)
'Dynamite' was a trade name introduced by Nobel for nitroglycerine adsorbed on Kieselguhr. Later, blasting 'gelignite' was developed by gelatinising nitroglycerine in 8% nitrocellulose. In the 1960s and early 1970s the amount of nitroglycerine in blasting gelignites was reduced and replaced with less expensive components such as dinitrotoluene and TNT. These explosives were hazardous to use and have largely been replaced by modern blasting explosives, although nitroglycerine-

based explosives are still manufactured (primarily for export) and constitute approximately 10% of the commercial explosives market.

Modern commercial secondary explosives are generally mixtures of ammonium nitrate with various fuels and sensitisers. The two most important types are slurry and 'ANFO' explosives. ANFO consists of a simple mix of ammonium nitrate and fuel oil. Porous ammonium nitrate granules are mixed with fuel oil to form a free-flowing explosive which is easily loaded into boreholes. Mixing generally takes place on site in large automatic blending and loading units. ANFO is one of the cheapest explosives available and is used particularly in open-pit mining.

Slurry explosives were developed for use specifically in water-containing boreholes because of their excellent water-resistant properties. They consist of an aqueous solution of oxidiser (primarily ammonium nitrate) containing dispersed sensitising fuel and excess solid oxidiser.

Fuels used in slurry explosives may include explosive compounds (eg TNT) or non-explosive materials, such as aluminium powder, hydrocarbons and cellulosic materials. Additional oxidants, eg sodium nitrate or sodium perchlorate, may be added in small quantities. Thickeners such as guar gum and cross-linking agents, such as borax, may be added.

Slurries lend themselves to efficient on-site mixing in pumping systems. Pre-mixed oxidisers and fuels are transported on site and mixed (generally in a paddle mixer) with gelling agents and cross-linking agents before being pumped into boreholes. Less commonly, plant-mixed slurries are prepared in ribbon-type mixers and packed into plastic sleeves prior to transportation to a distributor's magazine. On site they are extruded into boreholes by pressure-loading equipment.

In addition to ANFO and slurry explosives, emulsion explosives have been developed in recent years. These consist primarily of 'water-in-oil' emulsions of ammonium nitrate solution in a mineral oil phase. These have tended to replace the gelatinous ammonium nitrate-based explosives containing NG or EGDN (nitroglycol).

2.3.2 Propellants

Propellants are classified as solid or liquid. Gun propellants are always solid and are generally either single base for small arms or triple base for large guns. Rocket propellants may be solid (double base or composite) or liquid.

Nitrocellulose is the most widely used component of gun propellants. It is prepared by the nitration of cellulose (cotton or high quality cellulose from wood pulp). The crude product is stabilised by boiling and then neutralised by washing with hard water (or water plus a little chalk) before being pulped and blended.

Single base propellant consists primarily of NC, whilst double base is NC plus NG and triple base is NC and NG plus nitroguanidine as a flash suppressant.

Solid propellant: single base

In the manufacture of single base propellant, NC is gelatinised with the aid of solvents (generally ethanol, acetone or diethyl ether) and mixed with small quantities of various additives in an incorporator to form a 'dough'. Additives include: stabilisers, such as diphenylamine; modifiers to control the burning rate, such as methyl centralite (dimethyl diphenyl urea) or dibutylphthalate; plasticisers such as dinitrotoluene; flash-suppressing agents such as potassium sulphate. The dough is then shaped in an extrusion press and cut into the desired lengths. Residual solvent is removed by water steeping and oven drying. The dried powder is generally coated with graphite in drums to improve its flow characteristics.

Solid propellants: double base

In the manufacture of double base propellant, NG is added to an aqueous suspension of NC to form a paste, which is then de-watered. The dried paste is mixed with the additives in the incorporator and the dough is then gelatinised on hot rollers. The product is shaped by extrusion in a press. Alternatively, cast double base propellant, as used in rocket motors, is prepared by the addition of a casting powder (NC, NG and stabiliser) and a casting liquor (approximately 75% NG dissolved in triacetin) to a mould; it is then cured at the required temperature.

Solid propellants: triple base

Triple base propellant is manufactured by the incorporation of NC/NG 'paste' with nitroguanidine. A solvent (often acetone) is added to 'dough up' the mixture. After incorporation, the 'dough' is pressed as in the case of single base propellant and then dried in ovens.

Solid propellants: composite

Composite propellants consist essentially of an oxidiser (usually ammonium perchlorate) in a fuel matrix, either hydroxy-terminated polybutadiene (HTPB) or polyisobutylene (PIB). The oxidiser and fuel, together with small quantities of performance additives such as aluminium powder, are mixed in an incorporator. The older 'plastic' or 'thermoplastic' propellant containing oxidiser and PIB is a solid which softens at higher temperatures, enabling it to be shaped by extrusion. This has largely been superseded by 'rubbery' propellant, in which the mixture of oxidiser and HTPB is a fluid. A chemical additive (usually an isocyanate) causes cross-linking to occur and the cured fluid is cast into the required form and irreversibly converted to a solid.

Liquid propellants

The three principal types of liquid propellant are mono-propellant, bi-propellant and hybrid propellant. Mono-propellants consist of oxidiser and fuel in the same molecule, eg isopropylnitrate, whilst bi-propellants are usually liquid fuels and oxidisers filled into separate tanks in the projectile following manufacture. Bi-propellants generally find a greater application within the United Kingdom than mono-propellants. The most important fuels used include hydrazine and unsymmetrical dimethylhydrazine. The hydrazines are generally imported from the United States and stored in small quantities. Common oxidisers include inhibited red fuming nitric acid and nitrogen tetroxide.

Hybrid propellant systems utilise combinations of solid and liquid fuels and oxidisers but are currently only in experimental use in the United Kingdom.

2.3.3 Pyrotechnics

Pyrotechnics manufacture is normally a batch process, with the batch size varying from around 0.5 kg to tens of kilograms.

Depending on the product, manufacturing methods include:

dry mixing of powders by tumbling or sieving;
wet blending of ingredients in end runner or edge runner mills;
suspension of solids in solutions from which the product is precipitated.

Subsequent treatment can involve drying in air or in ovens, possibly under vacuum, or in fluid-bed driers.

2.3.4 Matches

Splints are made by peeling wood veneer (usually poplar or pine) in a lathe to a thickness of one match dimension and chopping it on a machine to the other two dimensions. The box is a one-piece component generated at high speed from a reel. In the early days of match manufacture, the splints were dipped into the head material in rows, held between slats in a hand frame, but today they are dipped by machine, first in molten wax and then the head material, before being dried and packed in controlled numbers.

2.4 Handling, storage and transfer of finished products

Commercial explosives are frequently prepared as non-explosive constituents and then mixed on site prior to use.

Military explosives may be transferred to a filling plant for the production of bombs and shells etc. This activity may occasionally be carried out on the manufacturing site, so that the final product is the actual munition. Military explosives are mostly stable and no chemical decomposition has been detected under normal service storage conditions (although TNT will turn noticeably dark brown if exposed to direct sunlight). NG and NC tend to decompose slowly, although this is minimised by the addition of stabilisers. Other explosives, notably pyrotechnics and some composite propellants, can be degraded by atmospheric water vapour.

Pyrotechnics in particular are frequently filled on the manufacturing site. Secondary explosives are generally transferred as powders or flakes to separate filling sites; NG and EGDN are oily liquids which are very sensitive to impact and therefore need careful handling.

Secondary explosives and pyrotechnics are transported either as filled stores or as bulk solids held in appropriately approved packaging. Gun propellants are generally packaged into sealed aluminium canisters, fibreboard drums or wooden boxes.

Transportation of primary explosives, which are particularly sensitive to shock and friction, is sometimes performed in rubberised cloth bags. Here the explosive is generally saturated with either water or a water/alcohol mix and cushioned with inert media to prevent frictional initiation.

Testing of the finished product may be carried out in a proofing range at the manufacturing site. This may take the form of the trial detonation of filled munitions or rocket motors, the firing of gun propellants or the burning of pyrotechnic compositions. Testing may be carried out within enclosed proof ranges, within closed vessels, or sometimes on an open area of the site.

2.5 Wastes

Waste explosive materials can pose a hazard either through their accidental deflagration or detonation or through their toxicity to humans, animals and plants. The significance of these hazards will depend to some extent on the nature of the waste, the environmental conditions under which the waste is present and the current or proposed use of the site. Most explosive materials possess significant potential toxicity; NG, EGDN, nitroguanidine and TNT could pose particular health risks in this respect.

Owing to the age and previous operating practices of many explosives manufacturing sites, waste management policies will have undergone considerable change during the lifetime of the facility. Sites involved in manufacturing and handling of military explosives received Crown immunity from prosecution. On-site storage and disposal of waste was significant during war years. Production wastes, contaminated building rubble and wastes from ancillary processes, including boiler ash, may have been disposed of in unlined waste-tipping areas. These materials may also have been used extensively on some sites for in-filling excavated areas, canals etc. There are also instances where munitions such as waste detonators were buried in particular areas of sites.

2.5.1 Process effluent

The manufacture of high explosives generates considerable volumes of liquid effluent consisting mainly of acids, organic liquids and water, containing small amounts of dissolved or suspended explosive. The effluent will generally be high in oxygen demand with high levels of nitrate and sulphate compounds. The volume of effluent produced from primary explosives manufacture is usually small and may contain metals such as lead or silver and reactive compounds such as azides. Liquid effluent is not produced in significant quantities by the manufacture of propellants and pyrotechnics, although the manufacture of NC and of nitroguanidine related to propellant manufacture can give rise to acid effluents of varying strengths.

On-site recycling is now commonly practised to recover mineral (nitric and sulphuric) acids and organic solvents such as acetone. However, in the past, when recovery was not carried out, losses of process chemicals (eg acids, TNT) were considerable.

Process effluent is generally treated by settlement to allow separation of the solid explosive. If acidic, the supernatant liquid is neutralised, producing lime-based residues before final discharge to sewers. Although no longer permitted, there may have been discharge directly into surface waters (rivers, ditches etc) in the past. Effluents from NG manufacture may be subject to different treatment processes specifically designed to decompose traces of NG.

2.5.2 Wastewater

Wastewater can result from the cleaning of buildings and of plant which contain explosives. The floors of process buildings are regularly hosed with wash-water to ensure that pockets of explosives do not accumulate and also to reduce the sensitivity of any explosive present.

The small amount of explosive suspended in wash-waters is treated by settling in save-alls prior to final discharge to surface waters. The low solubility of most explosive materials in water usually ensures that carry-over of explosives is negligible.

In the past, wash-waters may have been discharged untreated to soakaways, which could have led to isolated pockets of explosive contamination in soil and sediments.

2.5.3 Solid explosive waste

Solid waste comprises reject explosives (including propellants) which cannot be reformulated, explosives settled in save-alls and settling tanks, floor sweepings and packaging, and possibly clothing and cleaning materials contaminated with explosives.

Owing to the hazardous nature of solid explosives waste, the normal method of treatment is by open burning on site. Prior to transport to the burning ground, floor-sweepings may be stored in rubberised buckets or cloth bags in process buildings. NC is usually stored water-wet and primary explosives may be stored under oil.

The open burning of waste explosives, solvents, oils, contaminated paper waste and scrap metal has traditionally been carried out on the majority of explosives manufacturing sites. This is probably one of the major potential sources of ground contamination at such sites. Usually, waste explosives are spread in thin layers on metal trays or directly onto an ash or gravel surface. The wastes can also be placed on a wood fuel base and soaked with paraffin to promote burning. Primary and secondary burns are usually carried out to ensure maximum possible destruction of explosive materials.

After burning, the ash is sometimes dowsed with water, which can then soak to ground or flow to surface water. Dowsing waters may contain small amounts of unburnt explosives, heavy metals, ash, suspended solids etc. Residual ash may be left in situ or collected and disposed of at licensed facilities on site or sent off site to landfill.

Solid wastes may be stored in a variety of suitable drums or containers held in either purpose-built concrete bunds or in open areas where there is a possibility of direct contact with soil.

2.6 Ancillary processes

Ancillary processes usually associated with explosives manufacture include solvent recovery systems, acid production and recycling facilities, boiler houses and engineering maintenance activities. These activities can also result in wastes which may be flammable, toxic or corrosive.

Some sites may have used electrical equipment which might contain polychlorinated biphenyls (PCBs).

3. Contamination

The contaminants on a site will largely depend on the history of the site and on the range of materials produced there. Potential contaminants are listed in the Annex and the probable locations on site of the main groups of contaminants are shown in

Table 2. It is most unlikely that any one site will contain all of the contaminants listed. It is recommended that an appropriate site investigation be carried out to determine the exact nature of the contamination associated with individual sites.

3.1 Factors affecting contamination

General areas of potential soil contamination are likely to be associated with process buildings, with storage and transfer areas for product or raw materials. Contamination may also be present in or near waste storage areas, wastewater drainage systems and wastewater treatment plants. In particular, contamination may be present at areas in and around burning grounds, proofing ranges, waste tipping areas and surface water soakaways. These areas are likely to be present on sites with a long manufacturing history. Contamination may also arise from accidents, spillages or leaks from drains, sumps and tanks. Residues of materials present at derelict works may be released into the environment during redevelopment, demolition and clearance work and could be spread across the site.

Where surface waters are present, contaminants such as mineral acids and soluble organic compounds (eg nitroaromatics, phenols, alcohols) could be present at relatively high concentrations. Depending on the hydrogeology of the site, groundwater may also be at a similar risk.

3.1.1 Explosive contaminants

Contamination by explosive materials has been detected in the soil and in the ground and surface waters associated with explosives manufacturing sites. Although the integrity of handling procedures is normally high, contamination of soils from spillages and accidents can occur. In addition, past practices for waste management may have been less stringent than current procedures.

The soil is most likely to contain the following explosive compounds: NC, NG, PETN (pentaerythritol tetranitrate), nitroaromatics such as TNT, propellants and nitramines such as RDX. Primary explosive compounds and pyrotechnics may also be present although probably only in small quantities and in localised areas. The principal risks associated with the concentrations of the chemicals likely to be found on former explosives manufacturing works are toxic rather than explosive. NG, nitroguanidine and TNT are the most toxic.

The quantities of explosives may build up in sub-surface soil to such an extent that they can even become visible. In many cases, they can pose a toxicity hazard as well as an explosive risk.

Safe working practices and sampling procedures are essential for the analysis of soils from explosive sites. It is strongly recommended that the people investigating such sites have appropriate knowledge of the safety and environmental hazards associated with explosives and explosive devices. They should obtain all available information about previous investigations. Any written clearances which were issued during past site management should be examined carefully to ensure they were prepared by competent persons and that they adequately cover the expected risks. If contamination is significant, transport of samples for off-site analysis may be regulated by the Road Transport (Carriage of Explosives) Regulations 1989. Authorisation from HM

Inspector of Explosives may also be required for certain investigative or redevelopment works including sampling and laboratory analysis.

3.1.2 Non-explosive contaminants

Non-chlorinated organic solvents/compounds
These are used as large volume raw materials or as solvents, eg in re-crystallisation and purification processes.

Chlorinated organic solvents
These are not ingredients for explosive manufacture but may have been used in general cleaning operations and in laboratories.

Fuel oil, petroleum and hydrocarbons
Many explosives manufacturing sites have their own on-site boiler plants for steam generation which require the bulk storage of fuel oil or coal on site. The degree of contamination will depend upon the storage facility design and the type (ie mobility) of the hydrocarbons used. Hydraulic oils are extensively used in a number of processes (eg propellant extrusion) giving rise to potential contamination in these areas.

Polychlorinated biphenyls (PCBs)
Many facilities will have had their own electrical sub-stations which may have utilised PCBs. Contamination may occur as a result of the filling or dismantling of transformers containing PCBs.

Mineral acids
These are almost exclusively mixtures of nitric acid and sulphuric acid in various proportions, used in the nitration of raw materials to produce high explosives. The corrosive nature of acid-containing effluents will have considerable potential for causing failure of drainage systems and sub-surface tanks and sumps, resulting in leakages to soil. Plant in older works may have brick/cement bunds and floors which may be prone to acid attack. Owing to the buffering capacity of most soils, widespread acidification is not observed, with localised acid contamination being more common. Impact on surface or groundwater may, however, be significant.

3.2 Migration and persistence of contaminants

Contaminants within the upper soil layer may be removed by downward leaching, run-off, volatilisation, chemical transformation and plant uptake. Those in the lower soil layer are sometimes removed by biodegradation or downward leaching. Downward leaching of contaminants promoted by rainwater infiltration may lead to the contamination of groundwater. Migration in a horizontal direction with groundwater flow may then occur.

The migration of contaminants within the sub-surface environment may be retarded by adsorption, ion exchange and chemical precipitation. The higher the organic matter and clay content within the soil, the greater the degree of adsorption of organic compounds and the greater the reduction in the degree of contaminant migration. Thus the greatest degree of migration will occur in coarse-grained sands and in gravels containing little organic matter.

3.2.1 Explosive contaminants

Explosive materials dissolved in a liquid medium such as acid or solvent could migrate with the liquid through the soil profile. Explosives in particulate form are generally only sparingly soluble in water and are therefore of fairly low mobility. Examination of data for a range of explosives indicates that Tetryl is relatively immobile followed by, in order of increasing mobility, HMX, TNT, RDX and NG. NG and EGDN are considerably more soluble in water than other high explosives and may be significantly mobile (they may be only slightly less mobile than, for example, benzene). They may migrate considerable distances from the source of contamination. Seepage through soil will also be promoted by the liquid nature of NG and EGDN. There is evidence that NG and picric acid may be capable of permeating plastic water supply pipes.

Lack of mobility in the majority of particulate explosives may mean that adsorbed materials provide an ongoing source of groundwater contamination owing to desorption and continuous leaching during rainfall.

Particulate explosives adsorbed to soil particles may be spread over a wide area as wind-blown dust. Slurry and emulsion explosives may have significant mobility in soil, particularly in coarse-grained soils, due to their physical form.

Ammonium nitrate will be taken up by plants fairly rapidly. It should be noted that ammonium nitrate is used mainly as a fertiliser. However, ammonium and nitrate ions do migrate freely and can lead to unacceptable pollution when entering groundwater.

Natural biodegradation may result in the significant long-term removal of organic compounds. However, most explosive compounds seem to be relatively persistent in the environment (this is particularly true of NC). TNT may be biologically transformed into compounds such as diaminotoluene and nitrosamines, which may be more toxic or carcinogenic than the parent compound.

3.2.2 Non-explosive contaminants

Mineral acids will migrate within soil-water in the dissociated form, ie as the hydrogen ion and the corresponding anion (eg nitrate or sulphate). The buffering capacity of most soils tends to neutralise slight acidity. Dissolved nitrate and sulphate will migrate fairly freely through the soil.

The movement of metals through the soil is significantly retarded by the presence of clay minerals and organic matter. The solubility of some metals may increase under acidic conditions (eg. copper, zinc and lead). In other cases the relationship is more complex. For example, trivalent chromium is more soluble under acidic conditions, whereas the solubility of hexavalent chromium is increased under both acidic and alkaline conditions and arsenic may become more soluble at higher pH levels.

Most of the organic solvents likely to be encountered are volatile and have moderate to high vapour pressures which lead to direct loss to atmosphere from the soil surface. The water-soluble organics such as alcohols, acetone and phenol are prone to migration through the soil system and eventually to groundwater.

Other less soluble solvents such as toluene will also tend to migrate to the water-table. Chlorinated solvents are persistent and very mobile and are common pollutants in aquifers.

Biodegradation processes in soils can be influenced by a number of factors, namely moisture content, oxygen concentration and pH values, acting separately or in combination. For example low moisture content reduces microbiological activity, while high moisture content can reduce oxygen penetration and possibly lead to anaerobic soil conditions. Such conditions enhance the biodegradation of some materials, eg chlorinated compounds, while aerobic conditions are needed to biodegrade many oils. Also, low pHs tend to reduce the bacterial population and encourage fungal activity; at pHs lower than 5, microbiological activity is much reduced. The presence of heavy metals also inhibits micro organisms. Notwithstanding these factors, at high concentrations in soil, even relatively non-persistent compounds may not biodegrade readily.

It is possible that plant buildings and infrastructure were insulated with asbestos lagging, or asbestos cement sheeting was used in roofing or cladding. This waste asbestos material may be found in discrete dumps on the site where plant has been dismantled or is still associated with existing buildings and plant.

Polychlorinated biphenyls do not degrade. They are fat-soluble and can build up in food chains.

4. Sources of further information

4.1 Organisations

For further information concerning the explosives, propellants and pyrotechnics manufacturing industry in the United Kingdom, the following organisations and trade associations should be consulted:

British Pyrotechnists Association
Arlen House
Salisbury Road
Leicester
LE1 7QS

CBI Explosives Industry Group
Centre Poin103 New Oxford Street
London
WC1A 1DU

The United Kingdom Chemical Industries Association Limited
Kings Buildings
Smith Square
London
SW1P 3JJ

Society of Chemical Industry
14–15 Belgrave Square
London
SW1X 8PS

4.2 Sources of further information concerning the activities described in this profile

Austin G T. *Shreve's chemical process industries.* 5th Edition. London, McGraw-Hill, 1984.

Cook M A. *Science of industrial explosives.* Ireco Chemicals, 1974.

Dragun J. *The soil chemistry of hazardous materials.* Silver Spring, MD, USA, Hazardous Materials Control Research Institute, 1988

Eckroth D, Graber E, Klingsberg A and Siegel P M. *Kirk-Othmer concise encyclopaedia of chemical technology.* Chichester, John Wiley and Sons, 1985.

Fedoroff B T and Sheffield O E. *Encyclopaedia of explosives and related items.* Volume 5. New Jersey, USA, Picatinny Arsenal, 1972.

Hay I. *ROF — the story of Royal Ordnance Factories 1939–1948.* 1949.

Kaye S M. *Encyclopaedia of explosives and related items.* Volume 9. Dover, New Jersey, USA, US Army Armament Research and Development Command, 1980.

Meyer R and Kohler J. *Explosives.* 4th Edition. VCH, 1993.

Tooley P. *Chemistry in Industry,* 1971, 4, 161–191.

Watts H E. *The law relating to explosives.* London, Charles Griffin and Company Limited, 1954.

Site Investigation Steering Group. *Guidelines for safe investigation by drilling of landfills and contaminated land.* Site Investigation in Construction No 4. London, Thomas Telford, 1993.

Case related to investigations of sites at which munitions were produced and tested:

Paul V. *Bibliography of case studies on contaminated land: investigation, remediation and redevelopment.* Garston, Building Research Establishment, 1995.

Information on researching the history of sites may be found in:

Department of the Environment. *Documentary research on industrial sites.* DOE, 1994.

4.3 Related DOE Industry Profile

Engineering works: mechanical engineering and ordnance works

4.4 Health, safety and environmental risks

The Notes issued by the Chief Inspector of Her Majesty's Inspectorate of Pollution (HMIP) provide guidance for the processes prescribed for integrated pollution control in Regulations made under the Environmental Protection Act 1990. Of particular relevance is:

> **Her Majesty's Inspectorate of Pollution.** *Processes for the sulphonation or nitration of organic materials.* Chief Inspector's Guidance to Inspectors, Process Guidance Note IPR 4/12. London, HMSO, 1992.

The Control of Substances Hazardous to Health (COSHH) Regulations 1994 and the Management of Health and Safety at Work Regulations 1992 are available from HMSO. Information on relevant health and safety legislation and approved codes of practice published by HSE publications are available from Health and Safety Executive Books, PO Box 1999, Sudbury, Suffolk, CO10 6FS (telephone 01787 881165), as well as HMSO and other retailers.

Information on the health, safety and environmental hazards associated with individual contaminants mentioned in this profile may be obtained from the following sources:

> **Sax N and Lewis R.** *Hazardous chemicals desk reference.* New York, Van Nostrand Reinhold Company, 1987.
>
> **Verschueren K.** *Handbook of environmental data on organic chemicals.* 2nd Edition. New York, Van Nostrand Reinhold Company, 1983.
>
> **Howard P H.** *Handbook of environmental fate and exposure data for organic chemicals.* Vols I and II. USA, Lewis Publishers, 1990.

4.5 Waste disposal and remediation options

Useful information may be obtained from the Department of the Environment series of Waste Management Papers, which contain details of the nature of industrial waste arisings, their treatment and disposal. A current list of titles in this series is available from HMSO Publications Centre, PO Box 276, London, SW8 5DT.

Publications containing information on the treatment options available for the remediation of contaminated land sites, prepared with the support of the Department of the Environment's Research Programme, can be obtained from National Environmental Technology Centre Library, F6, Culham, Abingdon, Oxfordshire, OX14 3DB.

A full list of current titles of Government publications on all aspects of contaminated land can be obtained from CLL Division, Room A323, Department of the Environment, Romney House, 43 Marsham Street, London, SW1P 3PY.

Advice on the assessment and remediation of contaminated land is contained in guidance published by the Construction Industry Research and Information Association (CIRIA), 6 Storey's Gate, Westminster, London, SW1P 3AU.

Annex Potential contaminants

The chemical compounds and other materials listed below generally reflect those associated with the industry and which have the potential to contaminate the ground. The list is not exhaustive; neither does it imply that all these chemicals might be present nor that they have caused contamination.

Explosives manufacturing industry

Primary explosives

Metals and metal compounds	silver, lead, magnesium mercury fulminate was important historically
Inorganic compounds	nitrite, nitrate and sulphate ions
Explosives	azides - silver and lead azides lead styphnate tetrazene

Military secondary explosives

Acids	nitric sulphuric acetic
Organic solvents	acetone ethanol cyclohexanone
Organic compounds	hexamine toluene mononitrotoluene dinitrotoluene polymers glycerine phenol anilines aldehydes organic esters acetic anhydride guanidine nitrate dicyanodiamide
Fuels	liquid hydrocarbons
Inorganic compounds	ammonium nitrate sodium nitrate potassium nitrate sodium sulphite sodium perchlorate potassium perchlorate

Explosives	TNT - 2,4,6-trinitrotoluene RDX - cyclotrimethylene trinitramine HMX - cyclotetramethylene tetranitramine picric acid - 2,4,6-trinitrophenol nitroguanidine tetryl - trinitrophenylmethylnitramine PETN - pentaerythritol tetranitrate NG - nitroglycerine
Metals found on proofing ranges	lead copper

Commercial secondary explosives

Organic compounds	mineral oils[1] dinitrotoluene[2] waxes
Fuels	liquid hydrocarbons[1]
Inorganic compounds	ammonium nitrate[1] aluminium powder[1] borax sodium nitrate[1] potassium perchlorate nitrate ions[1,2]
Explosives	TNT - 2,4,6-trinitrotoluene[1,2] RDX - cyclotrimethylene trinitramine[1] EGDN - nitroglycol[1] NG - nitroglycerine[2] NC - nitrocellulose[2]

[1] Ammonium nitrate-based explosives
[2] NG-based explosives

Propellants, pyrotechnics and match manufacturing industries

Propellants

[3] Solid propellant - single, double and triple base
[4] Solid propellant - composite
[5] Liquid propellant

Acids	nitric[3,5] sulphuric[3]

Organic solvents	acetone[3] ether[3] ethanol[3] diethyl ether[3] ethyl carbonate (solvent for NC)[3] triacetin[3]
Organic compounds	diphenylamine[3] dinitrotoluene[3] diphenylamine[3] isopropyl nitrite and nitrate[5] ethyl centralite (diethyl diphenyl urea) glycerine
Inorganic compounds	potassium sulphate[3] nitrate ions[3,4,5] sulphate ions[3] ammonium perchlorate[4] ammonium, perchlorate ions[4] aluminium[4]
Fuels	unsymmetrical dimethylhydrazine[5] polyisobutylene (PIB)[4] hydroxy-terminated polybutadiene (HTPB)[4]
Explosives	NC - nitrocellulose[3] NG - nitroglycerine[3] nitroguanidine[3] ammonium picrate

Pyrotechnics

Metals and metal compounds	magnesium, aluminium, strontium, copper, titanium, bariummercuric thiocyanateantimony sulphidearsenic disulphide
Non-metals	boron, phosphorus (eg red phosphorus)
Inorganic compounds	nitrates, chlorates, perchlorates and chromates, usually of the alkaline and alkaline earth metals potassium dichromate, potassium perchlorate, ammonium nitrate
Organic compounds	waxes ammonium picrate

Matches

Paraffin
Potassium chlorate
Potassium dichromate
Ammonium phosphate
Tetraphosphorus trisulphide (phosphorus sesquisulphide)
Sulphur
White and red phosphorus
Ammonium thiocyanate

General contaminants

Fuel oils, petroleum
Hydraulic oils
Polychlorinated biphenyls (PCBs)
Asbestos
Chlorinated organic solvents
Metals (chromium, nickel, zinc)
Calcium used for wastewater treatment

Table 2 Main groups of contaminants and their probable locations

Chemical works: explosives, propellants and pyrotechnics manufacturing works

Main groups of contaminant	Location												
	Process buildings and building fabric	Production lines including blending tanks	Chemical storage areas (raw materials and products	Transfer areas	Pipework and pumps	Drainage systems	Waste storage	Waste water treatment areas	Site waste disposal and effluent lagoons	Proofing ranges and burning grounds	Solvent/ acid recovery plants	Boiler houses	Electricity substations and transformers
Explosive materials	▨		▨	▨		▨			▨	▨			
Acidic effluent and explosive residues					▨ N,A						▨		
Mineral acids		▨ N	▨	▨	▨						▨		
Non-chlorinated organic solvents/ compounds		▨	▨					▨			▨		
Chlorinated organic cleaning solvents	▨	▨	▨				▨				▨		
General inorganic salts	▨		▨				▨		▨				
Inorganic compounds	▨		▨	▨	▨	▨			▨	▨			
Calcium as lime								▨					
Metals and metal salts	▨	▨	▨						▨	▨ Pb, Cu		▨	
Non-metals, eg sulphur	▨	▨ S	▨						▨				
Asbestos	▨	▨					▨ Stm					▨	
Fuel oil	▨		▨					▨				▨	
PCBs													▨

N Nitration plant
Pb Lead

A Acid recovery plant
Cu Copper

S Sulphur in oleum plant
Stm Steam mains

Shaded boxes indicate areas where contamination is most likely to occur.

Recycled paper

DOE Industry Profiles

Airports
Animal and animal products processing works
Asbestos manufacturing works
Ceramics, cement and asphalt manufacturing works
Chemical works: coatings (paints and printing inks) manufacturing works
Chemical works: cosmetics and toiletries manufacturing works
Chemical works: disinfectants manufacturing works
Chemical works: explosives, propellants and pyrotechnics manufacturing works
Chemical works: fertiliser manufacturing works
Chemical works: fine chemicals manufacturing works
Chemical works: inorganic chemicals manufacturing works
Chemical works: linoleum, vinyl and bitumen-based floor covering manufacturing works
Chemical works: mastics, sealants, adhesives and roofing felt manufacturing works
Chemical works: organic chemicals manufacturing works
Chemical works: pesticides manufacturing works
Chemical works: pharmaceuticals manufacturing works
Chemical works: rubber processing works (including works manufacturing tyres or other rubber products)
Chemical works: soap and detergent manufacturing works
Dockyards and dockland
Engineering works: aircraft manufacturing works
Engineering works: electrical and electronic equipment manufacturing works (including works manufacturing equipment containing PCBs)
Engineering works: mechanical engineering and ordnance works
Engineering works: railway engineering works
Engineering works: shipbuilding, repair and shipbreaking (including naval shipyards)
Engineering works: vehicle manufacturing works
Gasworks, coke works and other coal carbonisation plants
Metal manufacturing, refining and finishing works: electroplating and other metal finishing works
Metal manufacturing, refining and finishing works: iron and steelworks
Metal manufacturing, refining and finishing works: lead works
Metal manufacturing, refining and finishing works: non-ferrous metal works (excluding lead works)
Metal manufacturing, refining and finishing works: precious metal recovery works
Oil refineries and bulk storage of crude oil and petroleum products
Power stations (excluding nuclear power stations)
Pulp and paper manufacturing works
Railway land
Road vehicle fuelling, service and repair: garages and filling stations
Road vehicle fuelling, service and repair: transport and haulage centres
Sewage works and sewage farms
Textile works and dye works
Timber products manufacturing works
Timber treatment works
Waste recycling, treatment and disposal sites: drum and tank cleaning and recycling plants
Waste recycling, treatment and disposal sites: hazardous waste treatment plants
Waste recycling, treatment and disposal sites: landfills and other waste treatment or waste disposal sites
Waste recycling, treatment and disposal sites: metal recycling sites
Waste recycling, treatment and disposal sites: solvent recovery works
Profile of miscellaneous industries incorporating:
    Charcoal works
    Dry-cleaners
    Fibreglass and fibreglass resins manufacturing works
    Glass manufacturing works
    Photographic processing industry
    Printing and bookbinding works

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