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EMISSION FACTORS FROM DEACTIVATION OF MUNITIONS, PART I

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1. ABSTRACT

Calculations and measurements are ~~at last~~ becoming available for the identification and concentrations of pollutants which result from the deactivation of most types of munitions. Open burning and detonation have been confirmed as environmentally sound for certain munitions. For recovery of metals from some munitions, the preferred deactivation methods involve incineration or chemical treatments.~~[43]~~ A catalog is being compiled for munition emissions. Energy recovery during deactivation has been demonstrated with a few highly energetic materials,~~[42,43]~~ And significant progress has been made in materials recycle and recovery.~~[44]~~ Details from the reports on energy and materials recovery are not repeated here.

2. EMISSION FACTORS FROM MUNITION DEACTIVATION METHODS

The term "emission factor" has a unique and useful meaning, namely the amount of emission per unit of starting material. Emission factors are expressed as pounds of emission per ton of starting material (or as kg per metric ton). Air emissions are a prime concern for incinerator flue gas, deflagration or open burning and open detonation (obod). Waste water emissions result from wet scrubbers in furnace systems, wash-out plants, chemical treatments, and cleanup. Emission factors from soil contamination are of concern with obod and deflagration.

Pollution which results from military operations concerns both the concentration of emissions and the absolute amount of emissions. Damage to environment and danger to health is mostly a function of the concentration of pollutants and particle size of particulates. But regulatory agencies also attempt to reduce the total amount even when the concentration is safe. Judgments of pollution control should be based on a case-by-case balance of the importance of the operation with cost and availability of state-of-the-art pollution control equipment, as well as with danger to health and environment. Open burning and detonation are the only methods available for disposal of certain munitions, and some of these cannot be stored indefinitely while awaiting development of other methods.

2.1. Incineration and Low-Temperature Open Burning

Aromatic nitro explosives such as TNT and ammonium picrate, which are burned in an incinerator at a rate of 300 lb/hr, or subjected to low-temperature open burning give up to 100 pounds of NO_x per ton, because of incomplete degradation. With proper combustion air feed rate, firing chamber design and temperature control, the NO_x emission factor from incineration can be reduced to 0.001 lb/ton or less.

Particulate emission factors in the final plume from the carbon, hydrocarbon fragments and organics alone can run as high as 100 lb/ton without pollution control. This can be reduced to less than 0.01 lb/ton by incinerators with cyclone and filter baghouse or scrubber, or by incineration with an afterburner. But if metals, inorganic salts or other compounds are part of the formulation in a munition to be deactivated, there may be a solid ash particulate remaining even with total degradation, depending on what the inorganic component is.[43]

With sufficient residence time in proper firing chamber conditions there will be no CO, Cl_2, HCN, C, organic fragments, carcinogens, or undegraded explosive. In practice, sufficient residence time is not always attained without afterburners. Particulates, including inorganic ingredients that go into the flue train as metal oxides, are usually separated by cyclones and filters.

In some processes such as incineration, RCRA will require the removal of 99.99% of POHCs present among the munition components. See Appendix VIII of 40 CFR 261, a section of RCRA, the Resource Conservation and Recovery Act. POHCs are the Principle Organic Hazardous Constituents. However, 99.99% removal may not always be good enough to satisfy other safety factors. For example, if bulk primer or a munition containing primer is deactivated in an incinerator at the rate of 300 lb/hr, then the remaining 0.01% of undegraded explosive will go into the pollution control equipment at the rate of 14 grams (1/2 ounce) per hour. The solid in the filter will also contain up to 18% combustible carbon black with such munitions. If a long-lived carbonaceous or tracer spark survives the few seconds to transit the entire length of the flue train it could easily start a fire in such a mixture of carbon and explosive in the filter residue. Baghouse fires have occurred during incineration of such material. If the 99.99% removal is attained by baghouse separation rather than by 99.99% degradation, the mixture of carbon black and other solid residue from the baghouse will contain still more explosive. Typical samples assay about 3% explosive. An afterburner eliminates both the C black and the organic residues including explosive and other POHCs from even being present in baghouse and cyclone residue.

Possible hazardous wastes from the incineration process for deactivation of small arms and projectile parts might be made up of the following, depending on the particular formulations and other specifications:

Gases: CO, NO_x, SO_2, HCl, PO_x, HCN, organic fragments, and vapors of Hg, Cd & Pb which subsequently condense to liquid or solid.

Particulates: Metal oxides (potassium, magnesium, aluminum, etc.), carbon and carbonaceous soot containing carcinogens, partly degraded and undegraded explosives or other components.

2.2. Deflagration

Some confusion has arisen from indiscriminate classification of open deflagration as open burning. Although it is a high temperature vigorous open burning, deflagration is an explosion, with the longest available residence time at high temperature degradative conditions of any common treatment. As such, open deflagration provides complete deactivation and total degradation. Open deflagration of oxygen deficient nitrocellulosic propellant has given 3.2 lb NO_x/ton. (See section on nitrocellulosic propellants.)

2.3. Detonation

The CO emission factor at the time of detonation may be as high as 1480 lb/ton for oxygen deficient explosives like the nitroaromatics, but with subsequent prompt oxidation of the CO to CO_2 within a few seconds. The CO emission factor for nitroglycerin, however, is zero, because it is an oxygen rich explosive, which means it contains more than enough internal oxygen to convert all C to CO_2 and H to H_2O without use of air oxygen.

2.4. Obod Emissions Study

Measurement attempts are now in the first stages to determine emission factors from open burning and detonation of many types of munitions and bulk explosives, by use of an instrumented helicopter. A few results are available for this presentation. A summary is also included for some past laboratory and detonation chamber measurements, and theoretical calculations, which have been proven dependable for the explosion state, but not representative of subsequent reactions in field conditions. Obod of some items such as nitrocellulosic propellants is non-polluting altogether.

3. BACKGROUND

3.1. Regulation, General Categories Versus Unaddressed Military Needs

Most open burning is to be eliminated by the Resource Conservation and Recovery Act (RCRA), but open burning and open detonation of explosives are allowed by RCRA,[39c] to provide a means of disposal for explosives, which cannot be disposed of by other methods. RCRA and other Environmental Protection Agency (EPA) regulations have yet to address some of the unique characteristics of the private and military explosives industries. However, EPA is now considering a solution to this need.

A proposed wording of a RCRA subsection to apply to propellants and explosives was submitted to EPA by the Department of Defense (DOD) in 1983. The EPA considered that specific wording was unnecessary for lack of enough explosives industry to warrant specific attention. Instead, EPA expects to publish a proposed section of 40 CFR 260 to cover all unique special cases, explosives included. This should appear toward the end of 1984.[40] It will be worded to give general guidelines, so that the pertinent environmental agencies can work on a case-by-case basis in mutual cooperation with the installation involved. This is intended to allow the greatest possible flexibility to the installation in addressing the unique situation of explosives, while satisfying the needs of disposal and simultaneous protection of health and environment. This can be successful only if the intended flexibility and mutual cooperation are not spoiled by wrong attitudes or lack of understanding on the part of either the industry or the regulatory authorities. The following paragraph is taken from the federal notice.[40]

"The planned standards would establish several environmental performance criteria, similar to 40 CFR 267 standards, that would be applied on a case-by-case basis in issuing permits. We believe that this approach will provide a flexible standard against which permits can be written. Under these rules, the owner or operator of each facility will do a site-specific environmental analysis against a set of environmental and human health criteria. This will enable the Agency to consider site-specific and waste-specific characteristics of each facility on their merits while providing full protection to human health and the environment."

3.2. Unique Properties, and Terminology of Explosives, Including: Burning, Combustion, Oxidation, Explosion, Deflagration, Detonation

Open burning, in terms of combustion and burning, is defined in RCRA[39c] mainly for application to environmental aspects of other industries, and does not handle the needs of the explosives industry. The terms 'burning' and 'combustion' have several connotations, and are sometimes used as exact synonyms. But to promote understanding in discussions of propellants, explosives and pyrotechnics (PEP), the terms should not be equivalent. For best PEP use 'burning' is a flaming process, and 'combustion' is a flaming oxidation reaction with air or oxygen. Whereas typical examples of burning are indeed flaming reactions with air oxygen, 'burning' is nevertheless not always chemical reaction with oxygen; indeed, burning is not necessarily 'combustion' at all. A jet of oxygen or air will burn smoothly in a room full of natural gas (methane), just as a jet of natural gas (such as a pilot light for a water heater) will burn smoothly in a room of air. These two examples are both combustion. But a jet of chlorine gas will burn smoothly in a room full of hydrogen gas, and so also will a jet of hydrogen gas burn smoothly in a room of chlorine gas. These two examples of burning are not combustion.

In the general sense, 'burning' is a flaming chemical reaction. Highly energetic chemicals, such as explosives, will usually burn smoothly without detonation. The flaming reaction may propagate by virtue of continous internal decomposition of the explosive chemical, without air combustion. In this case, burning of explosive in an incinerator or in the open is not necessarily combustion. If air is present, there will be some combustion just because the fuel is hot and in contact with oxygen, but this is an incidental side reaction, not needed for the flaming propagation. In some cases there is not even any incidental oxidation, which brings us to another unique aspect of explosives disposal, totally overlooked by RCRA. Flaming of explosives can be totally non-polluting, and simultaneously void of combustion. (Note that some schools have invented other narrow chemical uses of the terms oxidation and reduction, which have advantages for understanding certain chemical processes. For example, oxidation or reduction can mean: gain of an entity with low or high negative charge density; loss of an entity with high or low negative charge density; loss or gain of electrons; increasing or lowering level of oxidation state; gain or loss of a proton; gaining of an acidic or basic entity. This discussion is not concerned with such specific uses, but rather takes the more general definition: oxidation = combination with oxygen.)

Open burning of explosives is not always the stereotyped smoky bonfire in an open field. In PEP work some open burning is deflagration, which is a type of explosion. It is a high temperature vigorous flaming process. Although deflagration is an explosion it is not a detonation. (Detonation is an explosion in which the chemical reaction proceeds through the medium faster than the speed of sound.) Thus, open burning of a nitrocellulosic solid propellant on the ground is actually an explosion of the deflagration type, attaining a temperature of 5000 to 6000 degress F and lasting only one-half second per hundred pounds. This has been adequately demonstrated by the Ammunition Equipment Directorate (AED) at Tooele Army Depot, Utah (TEAD) in disposals of 50,000 to 100,000 pounds of outdated propellant daily for over a month, totalling over 2 million pounds. AED showed that the resulting white clouds were free of pollution to a greater degree than required by the Occupational Safety and Health Administration (OSHA) for worker breathing air supply. This type of disposal by open burning should preferrably be referred to as deflagration, to emphasize that it is not the stereotyped low temperature, drawn out burn with its typically polluting smoke. It is an explosion of low order, but does not qualify as detonation, because there is no shock wave. Open deflagration and open detonation in this sense are classed together as opposed to open burning. When proper understanding of the various types of open burning become common knowledge, non-polluting deflagrative open burning will not be hindered by false notions that all open burning is polluting.

Complete degradation of an explosive containing only carbon, hydrogen, nitrogen and oxygen, is the conversion of all the carbon to carbon dioxide, hydrogen to water, and nitrogen to diatomic nitrogen gas. The internal rearrangement of the atoms to utilize the self-contained oxygen within the structure to form water and carbon oxides can be properly called 'autocombustion'.

Two quotes on this subject now follow, taken from the Encyclopedia of Explosives and Related Items, volume 3, p D38, and volume 2, p B343 (3b, 2a respectively):

"The burning of deflagrating explosives usually proceeds rather violently and is accompanied by a flame (or sparks) and a hissing (or crackling) sound but not with a sharp loud report as in the case of detonating explosives... 'Deflagration' is a mode of explosion distinguished from detonation and consitituting the very rapid autocombustion of particles of explosive as a surface phenomenon."

"Burning in common usage is defined ... as a combustion in which material is consumed by fire resulting from interaction of the material with atmospheric oxygen at high temperature and accompanied by flame and sometimes sound... The term combustion implies the process of burning and in the popular mind is generally associated with the production of flame. So far as terrestial conditions are concerned, combustion is due to the combination of a combustible substance with oxygen and the consequent evolution of heat. The appearance of flame is due to the oxidation of gases or vapors at a very rapid rate so that high temperatures are obtained, the molecules involved thereby becoming very radiant. Scientifically, the term combustion has a broader meaning and is extended to other forms of oxidation...

"Combustion must be distinguished from deflagration, explosion and detonation."

To distinguish these differences in a manner most beneficial to the explosives industries, the common usage must be avoided, which equates burning and combustion, as explained in the first two paragraphs of 3.2.

4. CHEMICAL ASPECTS OF OPEN BURNING, OPEN DEFLAGRATION AND DETONATION (OBOD)

4.1. Thermodynamic and Kinetic Factors

Consider the following known thermodynamic equilibria of carbon monoxide:

$$\text{Heat} + C + CO_2 = 2CO$$

$$\text{Heat} + C + H_2O = CO + H_2$$

$$\text{Heat} + CO_2 = CO + 0.5\,O_2$$

In each case, increased temperature shifts the equilibrium mixture to the right, i.e., more carbon monoxide, less free carbon and carbon dioxide. In each equation, one volume of gas on the left goes to a greater volume of gas on the right; so increased pressure shifts the equilibrium mixtures to the left, i.e., increasing carbon dioxide and solid carbon while decreasing carbon monoxide.

Thermodynamic equilibrium and kinetics (the speed of reaction) are related in the following manner. For specified beginning concentrations of each entity, which are then allowed to react at a certain temperature and pressure, there will be a constant final concentration of each entity after equilibrium is eventually attained. This equilibrium may be a dynamic situation, in which the various entities are continuously changing into other entities present. But the concentration of any one form remains constant. The rate of decrease of any form equals the rate of its formation, at equilibrium.

Kinetics, on the other hand, has to do with how rapidly the final equilibrium concentrations are attained after the various concentrations, the temperature and pressure are first altered, or specified. Reactants may pass through an activated or complex intermediate state on the way to another final form. The activation energy barrier may be a strong barrier in one direction and a weak one in the reverse direction. The energy of detonation shock is supplied in such a short time that very strong barriers to reaction are overcome. The atoms within a molecule are actually dismembered from each other momentarily. Burning, with its gradual release of energy may not even approach this degree of activation. Mixtures of reactants in either case may be quenched before equilibrium is attained.

4.1.1. Open detonation case. Explosions which are conducted under conditions with any physical confinement such as in detonation chambers, demolition of buildings, etc., reflect the pressure inward and tend to delay its dissipation. But the heat from the high explosion temperature (5000-6000 degrees F or about 3000 degrees C), is rapidly absorbed by the confining materials and debris. Both the temperature and pressure effects tend to minimize the carbon monoxide ratio, and increase the free carbon in the equilibrium equations.

Unconfined, or so-called free explosions expose the reacting material to the much less dense medium of air in contrast to confining solids, and so retain the high temperature longer. The high pressure is dissipated sooner than in the confined case. Thus both the temperature and pressure effects maximize the carbon monoxide ratio and minimize the black carbon, in open-air detonations. Initial TNT products in detonation chambers typically show a $CO:CO_2$ ratio of 30:1 or more in explosions with less confinement and only about 2:1 in confined explosions. $CO:H_2$ ratio is about 3:1 with less confinement and 7:1 with confinement, trends which are in agreement with the given equilibrium equations and the principles discussed above. However, measurements following the initial blast in open air detonations indicate that the carbon monoxide is then oxidized to carbon dioxide.[33,34,36] If the foundation beneath the base of the material is not controlled, there may be more earthen dust thrown into the air from detonation than the amount of soot emitted from low temperature open burning. The shockwave may cause damage or initiate complaints if the location is not remote or provided with a sound muffling barrier. With proper choice of location, underlayment and barrier, detonation is often acceptable, whereas low temperature burning usually puts out serious pollution.

Even the longest of the relative durations of high temperature and pressure in the examples discussed above will not ensure complete chemical reaction of the explosive components with the surrounding air molecules, before the heat and pressure are dissipated. A chemical explosion is a fast reaction, one which generates energy much faster than it can be dissipated smoothly. The resulting pressure, heat, light, sound, chemical process, fragmentation, or radiation can be overwhelming. However, the fast evolution of energy propagates internal chemical changes that would not occur with gradual dispersion of the heat and pressure. Detonation is a high-order explosion, but has also been given a specific definition as a reaction which proceeds through the material faster than the speed of sound (0.33 kilometers, 0.21 miles, or 1100 feet per second at sea level).[32,39c]

Highly brisant explosives such as TNT, ammonium picrate and nitroglycerin cause the disruption of the bonds connecting the atoms within the molecules, to give momentary isolation of probably all the atoms in molecules so affected. This extreme condition is not because of the enormous energy release alone, but rather its application in a short time span to do work upon material in a narrow region of space. Hess[37] first defined brisance as the amount of work done by a unit weight of explosive per unit time. The high temperature of detonation -- 5000 to 6000 degress F -- lasts only a few seconds, and the sharp crest of the shock wave at about 3 million pounds per square inch passes in a fraction of a second. The atomized material rearranges, i.e., recombines with itself long before it can interact much with the surrounding air molecules. Furthermore, the mixture may or may not have time to equilibrate totally to the most thermodynamically favored forms for such high temperature and pressure, but a mixture representing a shift toward the favored equilibrium is quenched by the sudden loss of temperature and pressure extremes. Adiabatic expansion and convection then soon level the temperature and pressure to ambient values. Measurements made by AED following ignition of 4000-pound lots of propellant showed that ambient temperature was regained within 30 seconds. It is expected that detonation of equally large amounts of high explosive is also followed by recovery to ambient pressure and temperature rapidly. During the leveling period and thereafter, normal, slower chemical reactions of the detonation products with the atmosphere take place, such as oxidation of metals, hydration of oxides, and conversion of trace reactive organic species. Further reaction of nitrogen oxides proceeds slowly even if the mixture is quenched in nonequilibrium ratios of components.

Nitric oxide, NO, is indirectly hazardous, by conversion to nitrogen dioxide. This occurs in the atmosphere slowly by a mechanism totally different from the interconversion of NO and NO_2 in the extreme conditions of PEP disposal. As shown in the equilibrium equation, nitrogen dioxide, which is more stable than nitric oxide at 100 to 1000 degrees F, requires a net addition of energy to be converted to nitric oxide. Increased temperature therefore shifts the equilibrium in the following equation to the right, in favor of nitric oxide.

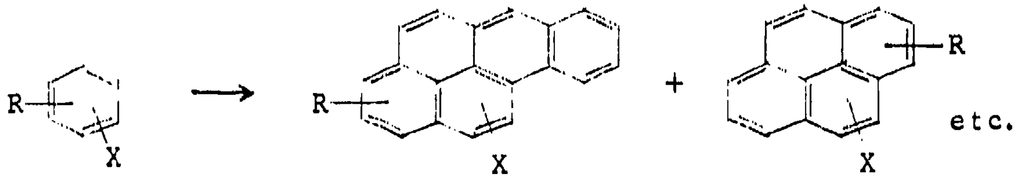
$$\text{Heat} + NO_2 = NO + 0.5\ O_2$$

At 1100 degrees F a mixture of NO and NO_2 at complete equilibrium is nearly void of NO_2, but at 275 degrees it is nearly void of NO. The most stable form of nitrogen is N_2, but if a detonation mixture is quenched it will contain some NO and NO_2. About 0.001 pound of total NO_x results from deflagration of one pound of high explosive or propellant. NO_x following detonation is mostly from the nitrogen within the explosive itself. But with open burning, there is slightly more NO_x from incomplete decomposition, and from reaction with air due to the longer reaction time.

4.1.2. Deflagrative open burning. Extremely high temperatures (5000-6000 degrees F) and long burn times (5 to 10 seconds per ton) compared with incineration, give open deflagration a marked advantage, because polluting emissions are slight or nil, such as in the deflagrative open burning of bulk propellants. See section on propellants.

4.1.3. Low temperature (non-deflagrative) open burning. Despite the high temperature and pressure of open detonation, a small amount of explosive may escape decomposition, and a small amount may be only partially degraded. But non-deflagrative open burning usually gives far more undegraded and partially degraded explosive than open detonation does. The heavy black soot produced by such open burning contains not only free carbon, but also many carcinogens and other hazardous constituents. The reason for this is clear from the kinetics and thermodynamics of the process. Open burning does not have the high pressure (2 to 3 million pounds per square inch incident with detonation. Explosives ordinarily burn slowly, but localized confinement of a portion may occasionally lead to detonation, because the gases released in confinement build up pressure, and the heat released cannot be dispersed quickly enough to avoid extremely high pressure and temperature. The normal low temperature burning takes place 2000 to 4000 degrees F cooler than open detonation. Furthermore, the propagating energy which gives the burn its continuation is supplied sufficiently well by the decomposition of the highly energetic chemical structure of the explosive, although some combustion with the air oxygen can occur because of its immediate availability and the long reaction time. These factors of non-deflagrative open burning: no high pressure, the lower temperature, and the propagating energy source are next compared in detail to the conditions of open detonation.

There is the absence of catalytic shock to dismember the atoms toward further reaction. The absence of the pressure wave tends to increase CO and decrease C. But the lower reaction temperature has an even greater effect in the opposite direction. With the propagation energy being independent of air combustion, the result is partial degradation with incomplete oxidation of the hydrocarbon fragments. Thirdly, those explosives with an oxygen deficiency tend to burn as though in a reductive flame, like the cool yellow flame of an acetylene torch without sufficient oxygen. This also gives a very sooty smoke containing carcinogenic fuzed ring aromatics and numerous exotic, hazardous constituents, such as imino-, nitroso- and other pi-bonded structures.



Aromatic ring with substituents

Benzpyrene and other carcinogenic fuzed-ring structures

Once formed, the carbonaceous soot is very slow to oxidize, even though thermodynamics show it will give more stable products. The reaction rate in getting there is very slow for a heterogeneous reaction. Heterogeneous here means that the reactants are not all in the same phase, or state of matter: solid, liquid or vapor. The carbonaceous soot is no longer in a highly energetic condition, as was the original explosive, and does not sustain a flame to overcome the activation energy barrier. It does not easily supply vaporous fragments to give a homogeneous reaction with oxygen.

Carbon and carbonaceous soot are very good insulators of heat, thus slowing transfer of the lesser heat still remaining, and preventing it from initiating the desired chemical reactions toward complete degradation.

Low temperature open burning, therefore, has at least five major factors which oppose attainment of the desired complete reactions. Open detonation gives near total degradation, carbon monoxide being the only substantial pollutant, and only in detonation of oxygen deficient explosives. Low temperature open burning gives substantial carbon monoxide with such explosives, along with numerous other hazardous products. Detonation of oxygen deficient explosives, as mixtures with oxygen rich explosives or added oxidants, overcomes the formation of carbon monoxide. Nitroglycerin and related explosives have excess oxygen. Peroxides and perchlorates are good additives, which, however, may produce salt or oxide particulates in the emission clouds.

4.2. Measurement and Theoretical Calculation of Emissions from PEP

Theoretical calculations have been made for the expected emissions from detonation and burning of explosives. Such information has been calculated by several authors on the basis of thermodynamics, kinetics, equations of state and known chemical behavior (e.g., 8, 21, 38). Actual analyses of the product have been made from deflgrations conducted on a small scale under laboratory conditions, in autoclaves and in detonation chambers designed to simulate field conditions (see references cited in 4.2. to 4.5.). There is good agreement of the main products and their amounts, as well as the principles involved. Many minor products have been identified which are present in only a few parts per million or parts per billion. The measured and predicted abundances of trace products differ according to the methods used. And until the last few years the technology has not been available to make accurate measurements of the explosion products in the atmosphere following actual field operations with large amounts of explosives. Explosives authorities have acknowledged the need for better sampling methods and more sensitive instruments. The complexity of the chemical processes inolved in explosions vary with many subtle factors. The following statements are taken from an authoritative 1958 publication of the American Chemical Society.[21]

"Unfortunately, the experimental measurement of the actual composition of the detonation products in field application is not possible by present methods... The products of detonation one measures in (laboratory) instruments depend critically on the loading density, the mode of initiation, confinement, whether the gases expand adiabatically and reversibly, freely, or against light burdens, and even on the chemistry of the surrounding medium."

The U.S. Bureau of Mines has categorized explosives permissible for use in coal mining according to the amount of poisonous fumes emitted per 1.5 lbs of explosive as measured in a certain autoclave method allowing the gases to expand freely without doing work, and then cooling slowly by heat transfer. Class A represents the generation of less than 2 moles of poisonous gas per 1.5 lbs of explosive, class B up to 4 moles, and class C (now discontinued) up to 6 moles. Few commercial explosives in use generate as much as 2 moles in actual field conditions. AED measurements and calculations indicate that less than 1 mole of total NO, NO_2, CH_4, NH_3, and HCN is expected from 1.5 pounds of most common explosives under field conditions. The amount of CO generated can be 10 moles or more per 1.5 lbs if the explosive is highly oxygen deficient (like TNT -- 70% deficient) and has a low packing density. (The classes of permissibles referred to here do not coincide with DOT designations of class A, B, and C explosives.) Besides these gases there is sometimes a measurable amount of undegraded explosive present among the products of detonation and burning, but not usually of deflagration. Some explosives are toxic, especially when inhaled as dust suspended in air. The small amount that sometimes exists from open detonation is well dispersed to insignificant concentrations, within a few seconds of fire ball and cloud expansion.

During the last few years mass spectrometry, microchromatography and other methods of analysis have become available or inexpensive enough for small industries to use in determining chemical emissions at parts per billion sensitivity, and in some cases at parts per trillion or better. Careful theoretical calculations are being confirmed by these methods and are more reliable than fume-gauge methods of measurement.

4.3. Propellants

4.3.1. Nitrocellulose (NC). Nitrocellulose also gives more polluting emissions with slow decomposition than with detonation or deflagration. Thermal decomposition without deflagration gives nitrogenous acids from the NO_x and moisture products, which then cause autocatalysis of accelerated decomposition with eventual transition to explosion (16b p308-309). With thermal decomposition up to 315 degrees F, as much as 50% or more of the nitrogen in the products can be in the form of NO_x.[27,28,29] Hydrogen cyanide, formaldehyde, and related substances are also produced initially (16b p317). Publications of Kast,[30] Rideal[31] and others summarized by Urbanski[16b] indicate the unique situation of nitrocellulose. It burns vigorously in the open with evolution of much heat, a mode of explosion properly called deflagration.[36] Such a deflagrative burn does not fit the usual characteristics of so-called 'open burning' (low temperature burning), as discussed in the section on thermodynamics. Low temperature burns can result from mixing the NC with sawdust or other dispersing flame suppressants, with the resulting noxious thermal decomposition products mentioned above, and the smoky flame typical of ordinary open burning. Detonation results from deflagration under confinement, which causes an exponential increase in reaction rate, from the undispersed heat and pressure buildup.[4b] Detonation of nitrocellulose gives little pollution, and open deflagration gives practically none besides carbon monoxide. Based on AED calculations, the amount of NO_x to be expected from open deflagration of one ton of nitrocellulose is 0.01 to 1 mg/m3 after 3 minutes with normal air conditions, and after 8 minutes with worst air conditions. The corresponding CO concentration is 1 to 25 mg/m3. In comparison, the OSHA breathing air standards for the workplace are 440 mg/m3 for CO, and 10 mg/m3 for NO_x (Short Term Exposure Limits = STEL).[41] The CO first formed in the deflagration quickly oxidizes to carbon dioxide as the medium cools to ambient and very little monoxide remains. Real time measurements in these plumes show CO to be some unknown value less than 0.5 ppm within a minute.

4.3.2. Ammonium perchlorate. Ammonium perchlorate is very insensitive and difficult to initiate as an explosive or propellant. It has 27% excess oxygen over that needed to give complete degradation, and it gives only gaseous products. For these reasons it is commonly used as an additive with other explosives. In the immediate oxidative environment present following explosion of ammonium perchlorate, the chlorine from the perchlorate is essentially all in the form of diatomic chlorine Cl_2. However, diatomic chlorine gas is not the final stable form of chlorine, which easily reduces to chloride ion in the form of hydrogen chloride, HCl, or chloride salts such as NaCl or KCl. Ammonium perchlorate and ammonium chlorate, as other perchlorates and chlorates, benefit from the presence of alkali metal salts in the formulation, which then provide a route for the chlorine to be converted to chloride without the formation of acidic hydrogen chloride gas. Either hydrogen chloride gas or solid suspension of chloride salts must be expected. The ambient concentration of chlorine gas in the atmosphere is zero, because it is converted so easily to hydrogen chloride. The nitrogen from ammonium perchlorate explosion is converted to nitrogen gas, N_2, and the hydrogen to hydrogen chloride and water. Organics from multibase PEP containing ammonium perchlorate are converted to water, nitrogen gas, and to carbon dioxide so long as the excess oxygen is still available. Inorganics present may add metallic salts or oxides, some of which are converted to hydroxides from the moisture present. Because they corrode gun barrels when used in small arms ammunition, perchlorates are used instead for pyrotechnics, blasting explosives, and propellant (20, p 91-2, p 230-2). High temperature deflagrating burns produce some nitrogen oxide, from conversion of the internal nitrogen and air nitrogen. Decomposition of ammonium perchlorate is catalyzed by the presence of transition metal salts and oxides (8, p P150-1). The concentration of the emissions is quickly dispersed to insignificant levels in detonation and deflagration, but not usually in low temperature degradation or burning.

4.4. Aliphatic (Non-aromatic Organic) Explosives.

4.4.1. PETN.

The explosive, pentaerythritol tetranitrate, PETN, ignites with greater difficulty than nitroglycerine upon contact with a flame,[26] and then continues burning at a very slow rate. Thermal decomposition at 410 degrees F gives a mixture which contains 70% nitrogen oxides.[24] Decomposition initiated by mechanical shock gives 30%. But initiation by detonation gives only 5%, along with he lowest total of $NO_x + CO$ of the three cases.

Again much less pollution is expected from open detonation in contrast to other mechanical initiation, and to either burning or thermal decompositions at low temperatures (<1000 degrees F).

4.4.2. RDX.

Thermal decomposition of RDX at temperatures up to 570 degrees F gives much NO_x and CO.[16c] Above 440 degrees F it ignites and decomposes within seconds. However, detonation gives mainly CO, CO_2, N_2 (nitrogen gas), water and a trace of hydrogen. Open burning of RDX is thus more polluting than open detonation, which has essentially only carbon monoxide to consider. AED calculations indicate that the CO will be oxidized to CO_2 quickly, leaving only insignificant CO concentrations within seconds following open detonation.

4.4.3. Nitroglycerin (NG).

Thermal degradation of nitroglycerin without detonation forms a small amount of nitric acid (16b, p 47), but detonation gives total conversion to water, nitrogen and carbon dioxide. The extremely clean detonation is due to the internal 5.88% excess of oxygen over the amount sufficient to convert all components to the totally oxidized forms. In work reported by Bowden and Yoffe,[24] nitrogen and carbon dioxide accounted for only 19.3% of the product composition if the NG was heated to 180 degrees C to initiate explosion, with the rest accounted for by nitric oxide NO, nitrous oxide N_2O, carbon monoxide CO and hydrogen H_2. These polluting side products were not present after initiation by detonation, but were present at 59.5% if the explosion was initiated by mechanical shock, in comparison with 80.7% after thermal initiation. (Side products may also be caused by other variations of the parameters and by unusual conditions of the testing mechanism, such as in bomb calorimeters, etc.). Side products may be formed in disposal of crude waste fractions from manufacture of nitroglycerin or munitions containing it. Here again, open burning gives noxious side products, which can be minimized or avoided by open detonation with a nitroglycerin supplement. Thus even nitroglycerin, which does not ordinarily produce carbon black in disposal, gives noxious products, such as formaldehyde[16b, 26] and others listed above with low temperature burning or thermal treatments or with insufficient initiation energy in explosions, etc, but it gives complete conversion to N_2, CO_2 and O_2 with no side products in proper disposal by open detonation.

The behavior of nitroglycerin to give polluting emissions from burning, but no pollution from strong detonation, is explained by evidence of two successive reaction stages.[25] The first of these is only slightly exothermic, with partial degradation. The second is highly exothermic, with total degradation to non-polluting products. It is not easily ignited, but once ignited it burns readily.[22] No detonation results if the material is not confined. With confinement, the gases build up pressure, which rapidly surpass the critical pressure to initiate detonation.

4.4.4. Nitroglycerin/nitrocellulose mixtures. In practice, oxygen-rich nitroglycerin (NG) is advantageously mixed with nitrocellulose (NC), giving explosives and propellants which explode to vapor with little or no polluting gases at all. Blasting gelatine is such a mixture with the oxygen excess of NG just balanced by the oxygen deficiency of NC. The mixture with 8% NC and 92% NG gives only carbon dioxide, nitrogen and water.[22] AED measurements of plume concentrations following deflagration of 4000-pound lots of 1:1.2:2 NG/NC/nitroguanidine propellant showed NO_x at 0.5 mg/m3 three minutes after the explosion, and CO at <0.5 mg/m3 after only 30 seconds. The amount of carbon monoxide (1700 mg/m3) initially formed by this 32.5% oxygen deficient mixture would disperse to 27 mg/m3 in 3 minutes. But the measurements show it is rapidly depleted to neglible concentration by air oxidation following the initial reaction.

4.5. Aromatic Explosives (See References 1 to 10)

Measurements of initial TNT products in detonation chambers (17 v3, ch 29; 18 ch 45; 16a 318; 38) typically indicate a $CO:CO_2$ ratio of 30:1 or more for free explosions and only about 2:1 in confined explosions. $CO:H_2$ ratio is about 3:1 in the open and 7:1 in confinement. However, carbon monoxide concentration is depleted or reduced drastically following the initial reaction in open air detonations.

Loading density of the explosive makes a difference in the ratio of detonation products, as shown by autoclave measurements and calculations based on well founded principles. For example, Schmidt[23] calculated that an increase of loading density of TNT from 1.0 to 1.59 g/cm3 lowered the CO/CO_2 ratio from 6.0 to 1.7, while giving a 46% increase in elemental carbon, and a 45% decrease of ammonia and hydrogen cyanide. Similar trends were observed for nitrophenols such as picric acid. Extensive calculations on various explosives were made more recently by Cook,[21] which confirm and broaden these observations.

A very significant behavior of the carbon monoxide from TNT has been observed.[33,34,36] Whereas the production of carbon monoxide is initially high from oxygen deficient explosives like TNT, as predicted by calculations and confirmed in bomb calorimeter and detonation chamber tests, measurements following free explosions indicate the subsequent conversion of the CO to CO_2. In such tests, no carbon monoxide is left at all, due to conversion with air oxygen as the heat and pressure disperse.

Other aromatic explosives behave similarly. Picric acid, picrates, etc., also burn with a sooty flame, but detonate in the open to much cleaner clouds.

5. TYPICAL INDUSTRIAL PRACTICE AND PREFERENCE

AED has communication with explosives industries throughout USA. The following summary represents their preferences and typical practices in disposal of rejected batches and other wastes that are not recycled. Incineration is sometimes used for PEP manufacturing waste, but is seldom preferred over detonation or deflagrative open burning.

5.1. Aromatic Explosives.

Detonation is much preferred. Burning and incineration give much black smoke, require as much or more attention, take too long, and cost too much. Incinerators with afterburners are effective but costly. Detonation gives little smoke or other pollutants.

5.2. Nonaromatic Explosives.

Detonation and deflagration are much preferred. Non-deflagrative burning does not give as much smoke as burning of aromatics, but is smokier, costlier and more inconvenient than detonation. Some types, such as inorganic blasting agents require a strong initiator to burn or detonate, but then give convenient and complete degradation. But residue mixed with sawdust or fuel gives a polluting burn.

5.3. Propellants.

Detonation or deflagration is much more preferred than low temperature burning (<1000 degrees F). Most propellants deflagrate well, taking about 6 seconds per ton, generating temperatures of 4000 to 6000 degrees F, and emitting very little if any pollution. Wastes in solvent or aqueous solution are best mixed with explosive or propellant for deflagration or detonation. Mixing with sawdust or fuel for burning is highly polluting, but is the only available method in some locations.

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