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Air



Detonation of Explosives; An AP-42 Update

Detonation of Explosives; An AP-42 Update

Pacific Environmental Services, Inc. 1930 14th Street Santa Monica, California 90404

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INTRODUCTION

As the title indicates, this report was written for inclusion in EPA Publication No. AP-42, <u>Compilation of Air Pollutant Emission Factors</u>. The work was performed under Work Assignment No. 12 of EPA Contract No. 68-02-2583.

11.3.1 General 1-5

This section deals mainly with pollutants resulting from the detonation of industrial explosives and small arms firing. Military applications are excluded from this discussion. Emissions associated with the manufacture of explosives are treated in Section 5.6, Explosives.

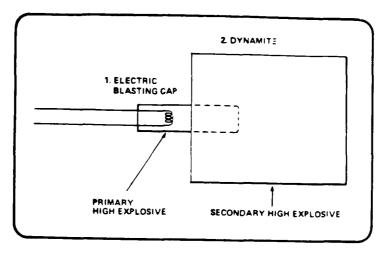
An explosive is a chemical material that is capable of extremely rapid combustion resulting in an explosion or detonation. Since an adequate supply of oxygen cannot be drawn from the air, a source of oxygen must be incorporated into the explosive mixture. Some explosives, such as trinitrotoluene (TNT), are single chemical species, but most explosives are mixtures of several ingredients. "Low explosive" and "high explosive" classifications are based on the velocity of explosion, which, in turn, is directly related to the type of work the explosive can perform. There appears to be no direct relationship between the velocity of explosions and the end products of explosive reactions. The end products are primarily determined by the oxygen balance of the explosive. As in other combustion reactions, a deficiency of oxygen favors the formation of carbon monoxide and unburned organic compounds and produces little, if any, nitrogen oxides. An excess of oxygen causes more nitrogen oxides and less carbon monoxide and other unburned organics. For ammonium nitrate and fuel oil mixtures (ANFO), a fuel oil content of more than 5.5 percent creates a deficiency of oxygen.

There are hundreds of different explosives, with no universally accepted system for classifying them. The classification used in Table 11.3-1 is based on the chemical composition of the explosives,

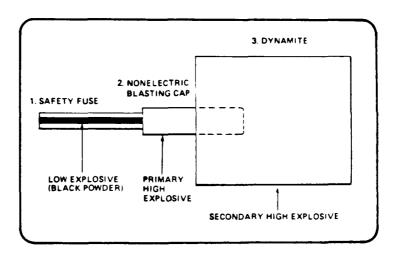
without regard to other properties, such as rate of detonation, which relate to the applications of explosives but not to the specific end products. Most explosives are used in two-, three-, or four-step trains that are shown schematically in Figure 11.3-1. To illustrate, the simple removal of a tree stump from the ground might be done with a two-step train made up of an electric blasting cap and a stick of dynamite. The detonation wave from the blasting cap would cause detonation of the dynamite. On the other hand, to make a large hole in the earth, an inexpensive explosive such as ammonium nitrate and fuel oil (ANFO) might be used. In this case, the detonation wave from the blasting cap is not powerful enough to cause detonation, so a booster must be used in a three- or fourstep train. Emissions from the blasting caps and safety fuses used in these trains are usually small compared to those from the main charge, because the emissions are roughly proportional to the weight of explosive used, and the main charge makes up most of the total weight. No factors are given in the next section for computing emissions from blasting caps or fuses, because these have not been measured and because the uncertainties are so great in estimating emissions from the main and booster charges that a precise estimate of all emissions is not practical.

11.3.2 Emissions and Controls^{2,4,5,6}

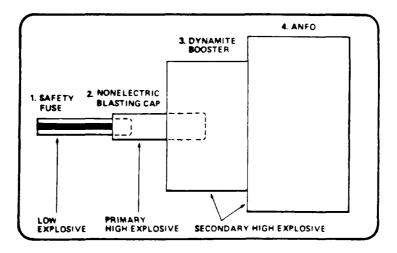
Carbon monoxide is the pollutant produced in greatest quantity from explosives detonation. TNT, an oxygen-deficient explosive, produces more CO than most dynamites, which are oxygen-balanced, but all explosives produce measurable amounts of CO. Particulates are produced as well, but such large quantities of particulate are generated by the shattering of the rock and earth which the explosive is used to move that the quantity of particulates from the explosive charge cannot be distinguished. Nitrogen oxides (both NO and NO2)



a. Two-step explosive train



b. Three-step explosive train



c. Four-step explosive train

Figure 11.3-1. Two-, three-, and four-step explosive trains

are formed, but only limited data are available on these emissions. Oxygen-deficient explosives are said to produce little or no nitrogen oxides, but there is only a small body of data to confirm this. Unburned hydrocarbons also result from explosions, but in most instances methane is the only hydrocarbon species that has been reported.

Hydrogen sulfide, hydrogen cyanide and ammonia have all been reported as products of explosives use. Lead is emitted from small arms ammunition when lead projectiles and/or lead primers are fired, however the explosive charge does not contribute lead to the emissions

The emissions from explosives detonation are influenced by many factors, such as explosive composition, product expansion, method of priming, length of charge, and confinement. These factors are difficult to measure and control in the field and are almost impossible to duplicate in a laboratory test facility. With the exception of a few studies in underground mines, most studies have been performed in laboratory test chambers that differ substantially from the actual environment. Any estimates of emissions from explosives use must be regarded as order of magnitude approximations that cannot be made more precise, because explosives are not used in a precise, reproducible manner.

To a certain extent, emissions can be altered by changing the composition of the explosive mixture. This has been practiced for many years to safeguard miners who must use explosives in underground mines. The U.S. Bureau of Mines has a continuing program to study the products from explosives and to identify those explosives that can be used safely in underground mines. Lead emissions from small arms use can be controlled by using jacketed soft point projecticles and special leadfree primers.

Emission factors are given in Table 11.3-1.

Table 11.3-1. EMISSION FACTORS FOR DETONATION OF EXPLOSIVES (EMISSION FACTOR RATING: D)

			Carbon Monoxide ^a		Nitrogen Oxides ^a		Methane ^b		Other ^a		
Explosive	Composition	Uses	kg/MT	1b/ton	kg/MT	1b/ton	kg/MT	1b/ton	Pollu- tant	kg/MT	lb/ton
Black powder ²	75/15/10; potassium (sodium) nitrate/charcoal/sulfur	delay fuses	85 (38-120)	170 (76-240)	unk	unk	2.1 (0.3-4.9)	4.2 (0.6-9.7)	H ₂ S	12 (0-37)	24 (0-73)
Smokeless Powder ²	nitrocellulose (sometimes with other materials)	small arms propellant	38 (34-42)	77 (6 8-84)	unk	unk	0.6 (0.4-0.6)	1.1 (0.7-1.5)	H ₂ S Pb	10 (10-11) c	21 (20-21) c
Dynamite, Straight ²	20-60% nitroglycerine/ sodium nitrate/wood pulp/ calcium carbonate	rarely used	141 (44-262)	281 (87-524)	unk	unk	1.3 (0.3-2.8)	2.5 (0.6-5.6)	H ₂ S	3 (0-7)	6 (0-15)
Dynamite Ammonia ²	20-60% nitroglycerine/ ammonium nitrate/sodium nitrate/wood pulp	quarry work stump blasting	32 (23-64)	63 (46-128)	unk	unk	0.7 (0.3-1.1)	1.3 (0.6-2.1)	H ₂ S	16 (9-19)	31 (19-37)
Dynamite, Gelatin ²	20-100% nitroglycerine	demolition, construction work, blasting in mines	52 (13-110)	104 (26-220)	26 (4-59)	53 (8-119)	0.3 (0.1-0.8)	0.7 (0.3-1.7)	н ₂ s so ₂	2 (0-3) 1 (0-8)	4 (0-6) 1 (1-16)
ANF04.5	ammonium nitrate with 5.8-8% fuel oil	construction work, blasting in mines	34	67	8	17	unk	unk	S0 ₂	1 (0-2)	2 (1-3)
TNT ²	trinitrotoluene	main charge in artillery pro- jectiles, mortar rounds, etc.	398 (324-472)	796 (647-944)	unk	unk	7.2 (6.6-7.7)	14.3 (13.2-15.4)	NH ₃ HCN C ₂ H ₂ C ₂ H ₆	14 (14-15) 13 (11-16) 61 0.5	29 (27-30) 27 (22-32) 121 1.1
RDX3	(CH ₂) ₃ N ₃ (NO ₂) ₃ cyclotrimethylenetrinitroamine	booster	98d (2.8-277)	196 ^d (5.6-554)	unk	unk	unk	unk	NH3	22 d (12-61)	44d (24-122)
PETN ²	C(CH ₂ ONO ₂) ₄ pentaerythritol tetranitrate	booster	1 4 9 (138-160)	297 (276-319)	unk	unk	unk	unk	NH ₃	1.3 (0-25)	2.5 (0-5)

a Based on experiments carried out prior to 1930 except in the case of ANFO, TNT and PETN

t The factors apply to the chemical species, methane. They do not represent total VOC expressed as methane. Studies were carried out more than 40 years ago.

c Greater than 6 g per 158 grain projectile (0.6 kg/MT, 1.2 lb/ton).

d These factors are derived from theorectical calculations--not from experimental data.

References for Section 11.3

- 1. C. R. Newhouser, <u>Introduction to Explosives</u>, National Bomb Data Center, International Association of Chiefs of Police, Gaithersburg, MD (undated).
- 2. Roy V. Carter, "Emissions from the Open Burning or Detonation of Explosives", Presented at the 71st Annual Meeting of the Air Pollution Control Association, Houston, TX, June 1978.
- 3. Melvin A. Cook, <u>The Science of High Explosives</u>, Reinhold Publishing Corp., New York, 1958.
- 4. R. F. Chaiken, et al., Toxic Fumes from Explosives: Ammonium Nitrate Fuel Oil Mixtures. U. S. Bureau of Mines Report of Investigations 7867, 1974.
- 5. Sheridan J. Rogers, <u>Analysis of Noncoal Mine Atmospheres: Toxic Fumes from Explosives</u>, Bureau of Mines, U.S. Department of Interior, Washington, D.C., May 1976.
- 6. A. A. Juhasz, "A Reduction of Airborne Lead in Indoor Firing Ranges by Using Modified Ammunition", Special Publication 480-26 Bureau of Standards, U. S. Department of Commerce, Washington, D.C., November 1977.

BACKGROUND DOCUMENT SECTION 11.3 DETONATION OF EXPLOSIVES

1.0 INTRODUCTION

The major reference document for this section was Reference 2, a literature survey prepared by R.V. Carter of the U.S. Army Environmental Hygiene Agency. This document deals with military explosives as well as those used by civilians. Some explosives are used in military and civilian applications, but the majority of military explosives are different from civilian explosives. The material in AP-42 Section 11.3 deals entirely with civilian explosives since it is believed that there would be little use of this document by the military. Accordingly, much of the material in Reference 2 is not included in Section 11.3 because it is not considered useful.

2.0 BLACK POWDER, STRAIGHT DYNAMITE, AND AMMONIA DYNAMITE

The factors for these explosives are taken from Table 4 in Reference 2 and were obtained, in turn, from the following, both published prior to 1930:

- A. Marshall, Explosives, <u>Their History</u>, <u>Manufacture</u>, <u>Properties and Tests</u>, Vol. I, 2nd ed., P. Blakestons's Son and Co., 1917.
- N. A. Tolch and G. St. J. Perrott, Dynamites: Their Propulsive Strength, Rate of Detonation, and Poisonous Gases Evolved, U.S. Bureau of Mines Report of Investigation 2975, 1929.

These factors are based on measured emissions and do not include any theoretically calculated emissions. Ranges are also given for each factor (from Table 4, Reference 2) to illustrate the variability of the results. Table 5 of Reference 2 also lists calculated emissions for ammonia from straight dynamite, but these have not been included in AP-42 because the agreement between measured and calculated emissions from detonation of explosives has frequently been poor (or at least unpredictable).

3.0 SMOKELESS POWDER

The factors for smokeless powder are taken from Table 4 in Reference 2 and were obtained, in turn, from the sources below - books that were published prior to World War II.

- Davis, T.L. <u>The Chemistry of Powder and Explosives</u>, Vol. I, New York: John Wiley and Sons, 1941.
- Faber, H.B. Military Pyrotechnics, Vol. 3, Government Printing Office, 1919.

The comments in the previous paragraph also apply to smokeless powder. In addition, the information on lead emissions from small arms firing was taken from Reference 6, which describes a modern study (1977). In Reference 6, no attempt was made to collect and measure all the lead emitted during firing. The gun was fired in an 80 liter chamber and a 20 liter sample of the contents was passed through a filter for subsequent lead determination. The fraction of lead sampled can be calculated as $1-e^{20/80}$ or .22 if the contents of the experimental chamber were well mixed at all times. Since this was not the case, the factors are given as >6 mg per 158 grain projectile, and the total amount per projectile is not estimated.

4.0 GELATIN DYNAMITE

The factors for methane and H_2S are taken from Table 4 in Reference 2 and were obtained, in turn, from the sources listed in

Section 2.0 above. The factors for CO, $\rm SO_2$, and nitrogen oxides are taken from Reference 5, Table 9, and are computed by averaging all values for nitroglycerine-based agents and water gels. Table 9 lists NO and $\rm NO_2$ separately, and these values were added together and presented as $\rm NO_x$ in Table 11.3-1.

5.0 AMMONIUM NITRATE/FUEL OIL (ANFO)

The factors for ANFO were taken from Reference 5, Table 9 (5.8% fuel oil) and from Reference 4, Tables 3 and 4 (6% and 8%fuel oil). Reference 4 also contains data for mixtures containing 1, 2, 3, and 4 percent fuel oil, but these were not used because it is believed that they do not represent mixtures that are commonly used. The data in Reference 5 includes emissions from the booster charge as well as the ANFO main charge. In Reference 4, the emissions from the booster charge (PETN) have been subtracted out. To derive the factors for Table 11.3-1, the emissions from the booster charge were added back in to the emissions from ANFO taken from Reference 4, using a weighting factor of 60 g booster per 430 g of main charge. These corrected emissions were then averaged with the emissions from Reference 5 to obtain the final References 4 and 5 list comparable emissions for CO, but Reference 4 gives somewhat lower NO_x emissions than does Reference SO_2 emissions are given only in Reference 5 and not in Reference The factors in Table 11.3-1 are straight averages of all relevant data without any attempt to judge the quality of individual data items and weigh some more heavily than others.

6.0 TNT, RDX, AND PETN

The factors for TNT are taken directly from Table 4 of Reference 2 which, in turn, were derived from the book by Marshall (listed

in Section 2.0 above) and the following:

 Ornellas, D.L. The Heat and Products of Detonation of Cyclotetramethylenetetranitramine, 2, 4, 6 Trinitrotoluene, Nitromethane and Bis [2, 2-dinitro-2-fluoroethyl] formal. J. Physical Chemistry 72:2390-2394, July 1968.

The factors for PETN were also taken directly from Table 4 for Reference 2 and were based on studies reported in the book by Marshall and also the following:

 Ornellas, D.L., J.H. Carpinter, and S.R. Gunn. Detonation Calorimeter and Results Obtained with Pentaerythritol Tetranitrate (PETN). <u>Review of Scientific Instruments</u> 37: 907-912, July 1976.

Both of the Ornellas studies were done in a small scale laboratory facility that may not be representative of actual use. No factors for RDX were given in Table 4 of Reference 2, so factors were taken from Table 5 of that same reference. Table 5 gives factors that are calculated theoretically, using methods described in Reference 3. The ranges given with each factor represent the results of making reasonable assumptions of ranges for values as input for the computations.

7.0 EMISSION FACTOR RATINGS

The ratings were made in a completely subjective manner. The explosive process is not reproducible: therefore there cannot be a precise factor to describe an imprecise operation. The values are based on experimental measurements (except for RDX), but many of the measurements were made more than 50 years ago using techniques that are crude when compared with modern methods. The factors are definitely better than mere guesses, but they are probably not high quality. Rather arbitrarily, they are rated D.

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16. ABSTRACT

This document contains the text of AP-42 (<u>Compilation of Air Pollutant Emission Factors</u>) Section 11.3, Detonation of Explosives. It discusses air pollutants resulting from the detonation of industrial explosives and small arms firing. Included are a process description, explosive train diagram, and a discussion of emissions. A background document which discusses, in some detail, the derivation of emission quantification methodologies follows the section itself.

17. KEY WORDS AND DOCUMENT ANALYSIS					
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Emission Factors Air Pollution Control Explosives Ammunition					
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