

Oxidizers / Peroxides





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Oxidation Potential

- Defined for our purposes as the ability to give up oxygen or cause “oxidation” of organic and inorganic materials.

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Oxidation Potential

- Compounds with high Oxidation Potentials may interfere with Oxygen Meters giving false high values.
- Oxidizing potential
 - $O_2 = 1$
 - $Cl_2 = 0.67$
 - Air = 0.21
 - $NF_3 = 1.56$
 - $ClF_3 = \text{OMG}$

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Oxidizers



- Any solid or liquid material that:
 - Readily yields oxygen or other oxidizing gas; or
 - That readily reacts to promote or initiate combustion of combustible materials; and
 - That can, under some circumstances, undergo a vigorous self-sustained decomposition due to contamination or heat exposure.

NFPA definition

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Oxidizers



DOT definition:

- a material that may, generally by yielding oxygen, cause or enhance the combustion of other materials.

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Enhancing Combustion

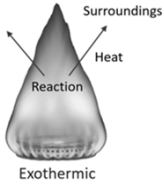
- [Diesel fuel fire video](#)
- Demonstration of diesel fuel fire (right)
 - vs
 - Diesel fuel with calcium hypochlorite added (left)



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Oxidizer Reactions

- Typically, oxidation-reduction reactions are exothermic, meaning that they release heat.
- Tend to undergo phase change to gaseous byproducts, substantially increasing pressure in closed containers.



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Common Features of Oxidizers

- Powerful reactive substances
- React with organic materials and other chemicals
 - Fuels
 - Lubricants
 - Greases and oils
 - Cotton
 - Animal and vegetable fats and bi-products
 - Coal
 - Straw
 - Sawdust
 - Wood shavings



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Recognize the Names

- Oxidizers have names that often include the terms:
 - “ite”,
 - “ate”,
 - “hypo”,
 - “per”,
 - “peroxy –” or
 - “– peroxide”

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Common Oxidizers

- bromine
- bromates
- chlorinated isocyanurates
- chlorates
- chromates
- dichromates
- hydroperoxides
- hypochlorites
- inorganic peroxides
- ketone peroxides
- nitrates

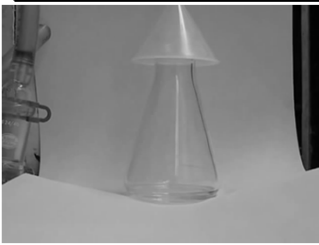
- nitric acid
- nitrites
- perborates
- perchlorates
- perchloric acid
- periodates
- permanganates
- peroxides
- peroxyacids
- persulphates



“ATES”

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Nitric Acid vs Ethanol



- 2 ml Ethanol
- 4 ml 67% nitric acid
- Does not always catch fire – but strong reaction and potential formation of ethyl nitrate – an explosive material

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Beirut – Ammonium Nitrate



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Common Oxidizers

OXIDIZERS

OXIDIZER

5.1

“ITES”

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Common Oxidizers

OXIDIZERS

OXIDIZER

5.1

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- perchlorates
- perchloric acid
- periodates
- permanganates
- peroxides
- peroxyacids
- persulphates

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Calcium hypochlorite
and
brake fluid

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Common Oxidizers

OXIDIZERS

OXIDIZER

5.1

“per”

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- perchloric acid
- periodates
- permanganates
- peroxides
- peroxyacids
- persulphates

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Chlorates and perchlorates are unstable molecules containing excess oxygen.

Are not flammable but will decompose rapidly when subjected to heat

Usually result in Mass Explosions

When they decompose

They release oxygen

Support rapid burning in any nearby combustible material

Heating Accelerates the Reaction

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Potassium Chlorate and Organics

postassium chlorate melting

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Oxidizers

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Common Oxidizers

OXIDIZERS



“peroxy”

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- nitric acid
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Common Oxidizers

OXIDIZERS



“peroxide”

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- perchloric acid
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- permanganates
- peroxides
- peroxyacids
- persulphates

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Sodium Peroxide



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Oxidizing Gases

- Air
- Oxygen
- Liquid Oxygen
- Chlorine trifluoride
- Nitrogen trichloride
- Nitrogen oxides (NO, NO2)

- Nitrogen Tetroxide
- Ozone
- Fluorine
- Chlorine
- Bromine trifluoride

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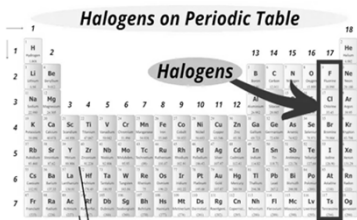
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Oxidizers

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Recognize the Names

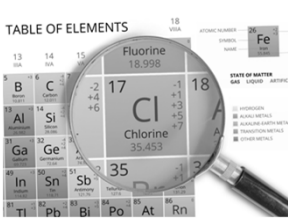
- Halogens are all strong oxidizers:
 - Bromine
 - Fluorine
 - Chlorine
 - Iodine



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Chlorine

- Complete combustion of methane in air generates carbon dioxide and water.
- However, burned in a chlorine environment, the combustion products are carbon tetrachloride vapor and hydrogen chloride gas



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Chlorine

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Classes of Oxidizers

- Class 1 Oxidizers:
 - slightly increase the burning rate of combustible materials.
 - do not cause spontaneous ignition when they come in contact with them.
 - Examples include aluminum nitrate, barium peroxide, certain concentrations of hydrogen peroxide (8-27.5%), nitric acid (40% or less), and sodium nitrate.

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Classes of Oxidizers

- Class 2 Oxidizers:
 - increase the burning rate of combustible materials moderately with which they come in contact.
 - may cause spontaneous ignition when in contact with a combustible material.
 - Examples of Class 2 oxidizers include specific concentrations of hydrogen peroxide, potassium permanganate, and calcium hypochlorite.

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Classes of Oxidizers

- Class 3 Oxidizers:
 - severely increase the burning rate of combustible materials with which they come in contact.
 - will cause sustained and vigorous decomposition if contaminated with a combustible material or if exposed to sufficient heat.
 - Examples include high-concentration hydrogen peroxide, perchloric acid, certain chlorates, and hypochlorites.

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Classes of Oxidizers

- Class 4 Oxidizers
 - can explode when in contact with certain contaminants.
 - can explode if exposed to slight heat, shock, or friction.
 - will increase the burning rate of combustibles.
 - can cause combustibles to ignite spontaneously.
 - Examples include specific high-concentration forms of hydrogen peroxide and perchloric acid, ammonium perchlorate, ammonium permanganate, guanidine nitrate, potassium superoxide, and tetranitromethane.

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Inorganic peroxides can act as both an oxidizer and a corrosive.

Hydrogen peroxide is an example of an inorganic peroxide

- Grocery store hydrogen peroxides are roughly 3 percent product with the remainder being water
- Commercial grade hydrogen peroxide can range from 30-70 percent product
 - Hydrogen peroxide in this concentration can spontaneously combust if mixed with Class A fuels (organic materials)

Peroxides may have the ability to combust and even explode in the absence of air

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Pool Peroxide (30%)



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Peroxide 70%



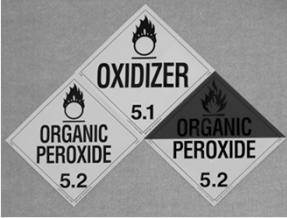
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Oxidizing agents can be categorized by their reactions.

Some are relatively stable

Some can be very unstable and even explosive

Oxygen is not a flammable element, but it can significantly accelerate combustion



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Organic peroxides are unique.

Typically contain both

- An O-O which supplies oxygen
- A part that can act as a fuel in its molecular structure

Just a small amount of heat may be needed to create a fire or explosion

Commonly used as catalysts and/or initiators for a polymerization reaction

May be liquids or solids

May be dissolved into solvents that may also be flammable

Are often shipped refrigerated and stored in cold storage cabinets

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Organic Peroxides

- Most organic peroxide formulations are fuels, not oxidizer
- The oxygen-oxygen bond only rarely decomposes to give free oxygen

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Organic Peroxides



- Maximum safe storage temperature (MSST)
 - The maximum storage temperature is the temperature below which the product can be stored safely, but at which it may lose assay if stored for long periods.
- Self accelerating decomposition temperature (SADT)
 - The lowest temperature at which product in a typical package will undergo a self-accelerating decomposition
- Emergency temperature
 - The Emergency Temperature is 10°C / 18°F below the SADT. Under no circumstances should products be exposed to temperatures at or above the emergency temperature.

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Temperature change in the product or container is an important clue indicating a reaction.



Organic peroxides should be stored below the maximum safe storage temperature (MSST) for routine purposes



Should organic peroxides reach the self-accelerating decomposition temperature (SADT), they undergo a chemical change and may violently release from their packaging



The length of time before this release depends upon how much the SADT is exceeded, which can greatly accelerate the decomposition

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During a SADT event the heat generated might autoignite flammable vapors.

Decomposition products may be much more toxic or corrosive than the original compound

After the material reaches its SADT threshold, there is generally a period of time before its decomposition becomes violent

Length of time depends upon how much the SADT is exceeded, which can greatly accelerate the decomposition

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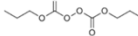
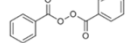
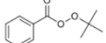
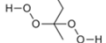
Most organic peroxides react to some extent with their decomposition products during thermal decomposition.

This reaction often increases the rate

Decomposition proceeds more rapidly as the decomposition products are generated

Monitoring equipment, will indicate when decomposition occurs

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Name	Typical Form	Structure	10 Hr Half Life (°C)	SADT (°C)
Di(n-propyl) peroxydicarbonate	Liquid with 40% diluent		50	-5
Dibenzoyl peroxide	Solid with 25% water		73	71
t-Butyl peroxybenzoate	Liquid neat		104	>60
Methyl ethyl ketone peroxide	Liquid with 60% diluent		N/A	63
2,5-Dimethyl-2,5-di(t-butyl)peroxy-3-hexyne	Liquid with 15% diluent		131	>80

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Decomposition - Peroxides

- Thermally induced decomposition
- induced to decompose by contaminants such as amines, metal ions (by themselves or because of contact with metal surfaces), strong acids and bases, and strong reducing and oxidizing agents.

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Types of Organic Peroxides



- Type A
 - Organic peroxide type A is an organic peroxide which can detonate or deflagrate rapidly as packaged for transport.
 - Transportation of type A organic peroxides is forbidden.

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Types of Organic Peroxides



- Type B
 - Organic peroxide type B is an organic peroxide which, as packaged for transport, neither detonates nor deflagrates rapidly, but can undergo a thermal explosion.

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Benzoyl Peroxide
25 grams
SADT 176°F



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Types of Organic Peroxides



- Type C
 - Organic peroxide type C is an organic peroxide which, as packaged for transport, neither detonates nor deflagrates rapidly and cannot undergo a thermal explosion.

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Types of Organic Peroxides



- Type D
 - Organic peroxide type D is an organic peroxide which -
 - Detonates only partially, but does not deflagrate rapidly and is not affected by heat when confined;
 - Does not detonate, deflagrates slowly, and shows no violent effect if heated when confined;
 - or
 - Does not detonate or deflagrate, and shows a medium effect when heated under confinement.

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Types of Organic Peroxides



- Type E
 - Organic peroxide type E is an organic peroxide which neither detonates nor deflagrates and shows low, or no, effect when heated under confinement.

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Types of Organic Peroxides



- Type F
 - Organic peroxide type F is an organic peroxide which will not detonate in a cavitated state, does not deflagrate, shows only a low, or no, effect if heated when confined, and has low, or no, explosive power.

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Types of Organic Peroxides



- Type G
 - Organic peroxide type G is an organic peroxide which will not detonate in a cavitated state, will not deflagrate at all, shows no effect when heated under confinement, and shows no explosive power.
 - – A type G organic peroxide is not subject to the requirements of this subchapter for organic peroxides of Division 5.2 provided that it is thermally stable (self accelerating decomposition temperature is 50 °C (122 °F) or higher for a 50 kg (110 pounds) package).
 - – An organic peroxide meeting all characteristics of type G except thermal stability and requiring temperature control is classed as a type F, temperature control organic peroxide.

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Arkema Chemical



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Peroxides may crystalize

- Crystals formed by peroxides may be shock, photo, heat or friction sensitive.





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Reactions

- What could go wrong

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Some oxidizers may break down and decompose based on their temperature.

- Reactions may be mild, violent, or explosive
- Many oxidizers are temperature-sensitive
- Some chemicals may be sensitive to high temperatures and some to low temperatures
- Information may be found in many chemical reference manuals

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PEPCON – Ammonium Perchlorate



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Texas City



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Oxidizer Characteristics

- Oxidizing materials can decompose readily at room temperature
- Incompatible materials include paper, wood, flammable and combustible chemicals, grease, waxes, cloth and many plastics that can act as a source of fuel

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Strategy and Tactics

- What is the state of the matter
 - Is it a liquid, solid or a gas
- Is it on fire / smoking / boiling / decomposing / fuming

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Solid Oxidizers

- Sweep up spills carefully with a broom and dustpan.
- Collect the material in a container with lid.
- Do NOT use anything that contains an organic material
 - Example: Anhydrous perchloric acid is highly unstable, explodes upon contact with organic material, and explodes spontaneously at room temperature after storage for a few days

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Liquid Oxidizers

- Clean up with inert absorbent pads
- If the liquid oxidizer is an acid, the spill should first be neutralized with sodium bicarbonate
- Dried acid residues can cause unexpected explosions in the future
- Do NOT use rags, paper towels, or sawdust to soak up
 - University of Iowa Example

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Fuming Nitric Acid



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Gas Oxidizers

- Spontaneous ignition may occur if a gauge or piping system is contaminated with hydrocarbons
- Cylinder leaks may lead to oxidizer-enriched environments that widen the flammable range of flammable gases and liquids at both the upper and lower flammable limits

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Gas Oxidizers

- Flash points and ignition temperatures may also be lowered; in the extreme case lowered to the point that a substance can ignite at room temperature

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Gas Oxidizers

- Clothing or other material that is exposed to oxidizer-enriched environments may become saturated, retaining the oxidizer for a minimum of 30 minutes, posing a threat for easy ignition and burning with great intensity
 - Note also that oxidizing gases are generally very toxic (except oxygen), so tissues such as lung, skin, and eyes are at risk

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Oxidizer Characteristics

- Intensification of fires of combustible materials
- Lower the flashpoints and ignition temperatures of combustible material
- Spontaneous ignition – no ignition source required
- Increase of flammable limits of organic materials
- Can form explosive mixtures
- Usually produces toxic fumes from fires or reactions
- Does not require atmospheric oxygen

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Oxidizer Characteristics

- Oxidation-reduction potential of the materials involved influences the intensity of the reaction
- Strong oxidizing agents plus strong reducing agents such as metals, metal hydrides or flammable organic solvents, fire or explosion is most possible
- Explosive potential can also be increased by exposure to heat, shock, or friction

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Strategy and Tactics

- If it is on fire - Identify the fire characteristics
 - Oxidizers tend to pop and crack – tossing debris out of the fire
 - Hot raging fires
 - Fires don't extinguish with normal technics

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CAUTION

- Oxidizers may not need air to support combustion. Removing a known air supply from a fire may not stop a fire involving oxidizers.

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Fires and Extinguishment

- Using the wrong type of extinguisher with certain oxidizer fires can result in a violent reaction or explosion (read section 5 on the SDS carefully)
- Typically smothering (sand, dirt) does not work
- Standard fire extinguishers may not work

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Fires and Extinguishment

- Halon or halocarbon typically react – toxic gases
- Dry powder with ammonia salts react with halogen containing oxidizers may react to produce NH_3
- Carbon dioxide does not work

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What Works

- Drenching amounts of water
- Blow the material apart with high pressure streams
 - Caution: non-miscible materials
- Heavy equipment to spread it out and then drench
- Let it burn – suffer the toxic fumes

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Strategy and Tactics - Peroxides

- Know the SADT and MSST (not always easy to find)
- TIC and temperature guns are my friend
- Understand the current conditions
- Risk based response
- Establish big enough control zones
- Confinement makes things worse

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Strategy and Tactics - Peroxides

- Understand the NFPA 704 Instability
- If the temperature is rising – make a decision
 - If the temperature approaches the MSST evacuate all personnel
- Demolition charges may be needed (195 Delaware)
- Dry ice and wet ice may be useful

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Spill Cleanup - Liquids

- Normally handled by spreading an inert absorbent material on the spill at a volume ratio of at least 2 to 1, then wetting down the mixture with water
 - sodium bicarbonate
 - calcium carbonate
 - clean sand
- Polypropylene based absorbent pads/berms can be used
- Sweep up and place in plastic drums, pails, or polyethylene bags
- Sweepings should be wetted down further

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Spill Cleanup - Solids

- Dilute with an inert absorbent and sweep up with broom
- Place in plastic drums, pails, or polyethylene bags
- Sweepings should be wetted down

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Spill Cleanup Hazards

- Fire (organic peroxides formulations may contain flammable solids and / or combustible liquids)
- Decomposition (due to either increased temperature or contamination)

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Spill Cleanup Hazards

- Evaporation of a safety diluent (either because the diluent is volatile at ambient temperature, or because the spill involved a hot surface)
- Increased worker exposure (peroxide formulations, especially hydroperoxides and ketone peroxides, can be strong irritants)
- Incorrect choice of absorbent material and/or methods

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Peroxide Fires

- Consult NFPA 400
- Water may be used to fight fires involving organic peroxides
- Effectiveness of water varies with the individual organic peroxide formulations
- Useful for heavier than water materials
- Water can aggravate control of fires or cause decomposition by heating

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Peroxide Fires

- Cool areas not yet involved in a fire
- When using hoses, spray or fog is most effective.
- For low boiling and low-density formulations AFFF foam may be more effective
- Runoff must be considered in the design of a firefighting approach.

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Common Types	Typical Formula	10 Hour Half-life Range (°C)
dialkyl peroxides	$R_1-O-O-R_2$	117-133
hydroperoxides	$R_1-O-O-H$	133-172
diacyl peroxides	$R_1-C(=O)-O-O-C(=O)-R_2$	20-75
peroxydicarbonates	$R_1-O-C(=O)-O-O-C(=O)-R_2$	49-51
peroxysalters	$R_2-O-O-C(=O)-R_1$	49-107
ketone peroxides	$H-O-C(=O)-O-O-C(=O)-H$	N/A
peroxyketals	$R_1-O-C(=O)-O-C(=O)-R_2$	92-115
alkylperoxy carbonates	$R_1-O-C(=O)-O-O-C(=O)-R_2$	90-100

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Health Hazards

- In general, oxidizers are corrosives and have similar health hazards to corrosives
- Contact with skin causes redness, irritation, and possibly burns

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Health Hazards

- Inhalation may cause respiratory tract irritation, sore throat, and possible burns. May lead to nausea, dizziness, drowsiness, headache, shortness of breath, rapid heart rate, pulmonary edema, or death

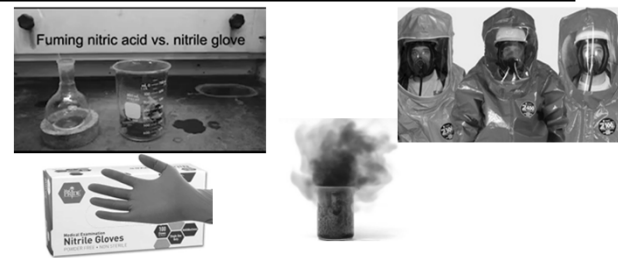
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Health Hazards

- Ingestion may cause severe digestive tract irritation, nausea, vomiting, and burns potentially leading to severe and permanent damage or death
- Chronic health effects are related to hematological and neurological changes. Absorption of some oxidizers has been associated with liver and kidney disease and cancer

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Know Your PPE



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Homemade explosive materials (HMEs) are typically made by combining an oxidizer with a fuel.

Components of Improvised Explosives		
Potential Fuels	Potential Oxidizers	Explosive Blends (Oxidizer + Fuel)
Hydrocarbons: Alcohol Carbon Black Charcoal Dextrin Diesel Ethylene Glycol Gas Kerosene Naphtha Ruin Sawdust Shells Sugar Vaseline Wax/Tarlin	Energetic Hydrocarbons: Nitrobenzene Nitromethane Nitrocellulose Elemental "Hot" Fuels: Powdered Metals - Aluminum - Magnesium - Zirconium - Copper Phosphorus Sulfur Arsimony Triulfide	Oxidizers: Perchlorate Chlorate Hypochlorite Nitrate Peroxide Iodate Chromate Dichromate Permanganate Sodium Chlorate Potassium Chlorate Ammonium Nitrate Potassium Nitrate Hydrogen Peroxide Barium Peroxide Ammonium Perchlorate Calcium Hypochlorite Nitric Acid Lead Iodate Sulfur Chlorate Potassium Permanganate Lithium Chromate Potassium Dichromate Nitrate Blends: ANFO (Ammonium Nitrate + Diesel Fuel) ANAI (Ammonium Nitrate + Aluminum Powder) ANS (Ammonium Nitrate + Sulfur Powder) ANIS (Ammonium Nitrate + Ising Sugar) Black Powder (Potassium Nitrate + Charcoal + Sulfur) Chlorate/Perchlorate Blends: Flash Powder (Potassium Chlorate/Perchlorate + Aluminum Powder + Magnesium Powder + Sulfur) Poor Man's C-4 (Potassium Chlorate + Vaseline) Armstrong's Mixture (Potassium Chlorate + Red Phosphorus) Liquid Blend: Hellbottle (Nitric Acid + Nitrobenzene)

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Homemade explosive materials (HMEs) are typically made by combining an oxidizer with a fuel.

Common Precursors Used To Make Explosives	
Precursors: Hydrogen Peroxide Sulfuric Acid (battery acid) Nitric Acid Hydrochloric Acid (muriatic acid) Urea Acetone Methyl Ethyl Ketone Alcohol (Ethyl or Methyl) Ethylene Glycol (antifreeze) Glycerin(e) Hexamine (camp stove tablets) Citric Acid (sour salt)	Nitrated Explosives: Nitroglycerine (Glycerine + Mixed Acid [Nitric Acid + Sulfuric Acid]) Ethylene Glycol Dinitrate (EGDN) (Ethylene Glycol + Mixed Acid [Nitric Acid + Sulfuric Acid]) Methyl Nitrate (Methyl Alcohol [methanol] + Mixed Acid [Nitric Acid + Sulfuric Acid]) Urea Nitrate (Urea + Nitric Acid) Nitrocotton (Gun Cotton) (Cotton + Mixed Acid [Nitric Acid + Sulfuric Acid]) Peroxide Explosives: Triacetone Triperoxide (TATP) (Acetone + Hydrogen Peroxide + Strong Acid [Sulfuric, Nitric, or Hydrochloric]) Hexamethylene Triperoxide Diamine (HMDT) (Hexamine + Hydrogen Peroxide + Citric Acid) Methyl Ethyl Ketone Peroxide (MEKP) (Methyl Ethyl Ketone + Hydrogen Peroxide + Strong Acid [Sulfuric, Nitric, or Hydrochloric])

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HME
Ammonium Nitrate,
Nitromethane,
Aluminum powder

Equivalent to 1 lb C4



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TATP and HMDT are dangerous at all stages of their manufacture, including as initial ingredients.

United States Department of Homeland Security

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Peroxide-Based Explosives Awareness

Peroxide-based explosives are commonly used in suicide operations

USE CAUTION:
PEROXIDE-BASED EXPLOSIVES ARE HIGHLY SENSITIVE TO:
HEAT
SHOCK
FRICTION

INDICATORS FOR LAW ENFORCEMENT:
POWDERY, WHITE SUBSTANCE
COOLING ON LAW EQUIPMENT
SUSPICIOUS PURCHASES OF
INGREDIENTS BELOW

INGREDIENTS:
TATP
- Acetone (nail thinner, nail polish remover)
- Hydrogen peroxide (disinfectants, hair bleaching agents)
- Strong mineral acids such as hydrochloric or sulfuric (batteries)

HMDT
- Hexamine fuel tablets (camping stoves)
- Hydrogen peroxide (disinfectants, hair bleaching agents)
- Weak acids such as citric

These materials are easily obtainable from chemical labs, hardware stores, beauty shops, and medical supply stores.

Bomber would likely transport peroxide-based explosives in a portable cooler and handle the material very delicately.

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TATP can look deceptively benign.

Is typically a white crystalline powder with a distinctive acrid smell



Can range in color from a yellowish to white color

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Summary Oxidizers

- Increase the rate of combustion
- Decompose with catalyst or heat
- Cause spontaneous ignition
- Cause explosive reaction



- shock sensitive

Manganese heptoxide

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Summary Oxidizing Agents



- Support combustion through oxygen or energy donation
- Unpredictable – can happen without warning
- Contamination with acid / base or with organics can lead to rapid decomposition.
- Strong oxidizing agents will also react violently with most organic compounds, powdered metals, Sulphur, phosphorus, boron, silicon, and carbon.

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