ATC

A SECTOR GROUP OF cefic

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Fuel Additive Packages containing 2-Ethylhexyl nitrate (2EHN)

Best Practices

MANUAL

Product Stewardship

Prepared by the ATC 2EHN Blends Work Group

ATC Document 86

Index

Section 1

Introduction

1.1 Fuel Additive Packages containing 2 ethylhexyl nitrate (2EHN)

2-Ethylhexyl nitrate (2EHN) is used to raise the cetane number of diesel fuels. This manual contains information which is intended to help users establish safe handling and storage procedures and systems for preparations (mixtures) containing 2EHN. These preparations, commonly known as fuel additive packages, may contain several other functional components and are marketed by additive producers to blenders of diesel fuels.

1.2 ATC 2EHN Blends Work Group

The ATC 2EHN Blends Work Group was formed in 2003 by the Technical Committee of Petroleum Additive Manufacturers in Europe (ATC), an affiliate member of the European Chemical Industry Council (CEFIC). It is comprised of those ATC members that are involved in blending fuel additive packages containing 2EHN with additional input from CONCAWE (the Oil companies' European association for environment, health and safety in refining and distribution).

The objective of ATC was to develop an industry guidance document covering the Health, Safety & Environmental aspects and best practices for handling fuel additive packages containing 2EHN. This manual is intended to provide you with information you may wish to consider when establishing safe storage and handling systems, with some guidelines for classification and labelling of such additive packages. We have applied conservative engineering judgement when recommending safety measures for blends containing 2EHN above certain concentrations. The ATC recommends that you should always refer to the latest product Material Safety Data Sheet or Safety Data Sheets (MSDS/SDS's) from suppliers as these are updated on a regular basis as new health and safety information becomes available.

1.3 Product Stewardship

ATC has a fundamental concern for all who manufacture and/or use 2EHN or fuel additive packages containing 2EHN. This concern is the basis for our Product Stewardship philosophy by which we assess the safety, health and environmental information on our products and take appropriate steps to protect employee and public health and our environment.

1.4 Customer Notice

ATC strongly encourages the users of fuel additive packages containing 2EHN to review their transportation, storage, use, and disposal of these products from the standpoint of safety, human health and environmental quality.

ATC believe the information and suggestions contained in this manual to be accurate and reliable as of the date of issue of this document.

However, since this document, furnished by ATC is provided without charge and since transportation, conditions of use and disposal are not within its control, ATC assume no obligation or liability of any kind for such assistance and do not guarantee results from use of such products or other information herein; no warranty, expressed or implied is given nor is freedom from any patent owned by ATC members or others to be inferred.

Information herein concerning laws and regulations is based on EU and North American regulations except when specific reference is made to those of other jurisdictions. Since conditions of use and governmental regulations may differ from one location to another and may change with time, it is the customer's responsibility to determine whether fuel additive packages containing 2EHN are appropriate for the customer's use, and to assure that the customer's workplace and disposal practices are in compliance with laws, regulations, ordinances, and other governmental enactment applicable in the jurisdiction(s) having authority over the customer's operations.

1.5 Legal Notice

This manual was prepared by the ATC. Neither the ATC nor any of its member companies, their employees, subcontractors, consultants, or other assigns make any warranty, expressed or implied, or assume any liability or responsibility for any use, or the results of such use, of any information, product, or process disclosed in this Manual, or represent that its use would not infringe on privately owned rights.

The Manual is intended to provide helpful ideas for those involved in the use of additive packages containing 2EHN. The Manual is necessarily general in nature and leaves dealing with product and site-specific circumstances to entities handling the product. The Manual is not designed or intended to define, create, or terminate legal rights or obligations.

The ATC, including any of its member companies, their employees, subcontractors, consultants, or other assigns, does not make any warranty or representation, either express or implied, with respect to the accuracy or completeness of the information contained in this Manual; nor does the ATC, including any of its member companies, their employees, subcontractors, consultants, or other assigns, assume any liability of any kind whatsoever resulting from the use of or reliance upon any information, procedure, conclusion, or opinion contained in this Manual, except to the extent such disclaimer of liability would be in violation of law in the jurisdiction of its use.

Although this manual follows the standard 16-section Material Safety Data Sheet (MSDS) / Safety Data Sheet (SDS) format for easy cross-reference to your supplier's MSDS/SDS, it shall not be used as an MSDS/SDS. Since fuel additive packages containing 2EHN may contain solvents and other functional components, readers should always refer to the supplier's latest MSDS/SDS.

Section 2

Composition

The amount of 2EHN in fuel additive packages varies depending upon the functional requirements of the specific additive package. Fuel additive packages are likely to contain hydrocarbon solvents and other components designed to impart specific functional properties to the package. Therefore, it is not possible to give information on the composition of individual fuel additive packages in this guidance document. For information on hazardous components in fuel additive packages, users should refer to the MSDS/SDS. Individual hazardous substances present at either 1% or 0.1% by mass (depending on the inherent hazard), or substances with a published Community exposure limit will be given in Section 2.

Section 3

Hazard Identification

Fuel additive packages are typically mixtures of several discrete components, each contributing to the overall hazard of the package. The potential hazards of the fuel additive package will therefore vary according to the nature and the concentration of the different chemistries present. The supplier MSDS/SDS should be consulted for potential adverse effects associated with the specific package. Potential adverse effects that can be attributable to 2EHN present in fuel additive packages are, however, described below.

3.1 Emergency Overview

2EHN in fuel additive packages can cause vasodilatation following exposure by inhalation or skin contact. Vasodilation leads to reduced blood pressure and other cardiovascular effects to produce such symptoms as throbbing headache, confusion and possible loss of consciousness. Fuel additive packages containing 2EHN may also present a possible aspiration hazard depending on the physical characteristics of the package.

2EHN is a self-reactive, energetic substance with a low auto-ignition temperature. If fuel additive packages containing 15% or greater 2EHN are heated above 100ºC, 2EHN may undergo a self-accelerating, exothermic decomposition that causes a rapid rise in temperature and pressure. Consequently, rupture of storage vessels, containers and equipment should be anticipated when pressure is generated by this thermal decomposition.

3.2 Potential Health Effects

3.2.1 Acute Health effects

Ingestion

Ingestion of fuel additive packages is not expected to be a primary route of exposure to 2EHN. Although ingestion is not thought to produce harmful effects (as classified under US, Canadian or European criteria) the material may still be damaging to the health of individuals with pre-existing medical conditions, especially if the ingested material is aspirated into the lungs.

Eye Contact

Although 2EHN is not classified as an eye irritant (according to US, Canadian or European criteria), direct contact with the human eye has been reported to produce transient discomfort as characterized by watering of the eyes and redness.

Skin Contact

Since 2EHN is readily absorbed through the skin, skin contact with fuel additive packages containing 2EHN may cause vasodilatation (leading to reduced blood pressure and other cardiovascular effects to produce such symptoms as throbbing headache, confusion and possible loss of consciousness). These effects are reversible following removal from the source of exposure (e.g. by washing the exposed area or removing contaminated clothing) and typically last for only a short period.

The substance is not classified as a skin irritant (according to US, Canadian or European criteria) but as with diesel fuel itself prolonged skin contact may produce temporary discomfort. There is no evidence of skin sensitisation associated with this material.

Inhalation

Inhalation of 2EHN vapours may cause irritation of the mucous membranes (nose, throat and lungs). In addition, absorption of 2EHN through the respiratory tract can result in vasodilatation (reduced blood pressure and other cardiovascular effects to produce such symptoms as throbbing headache, confusion and possible loss of consciousness).

All the above effects are reversible following removal from the source of exposure and typically last for only a short period.

3.2.2 Chronic Health Effects

There are no reports of chronic systemic effects associated with long-term exposure to 2EHN.

3.3 Environmental Hazards

2EHN is immiscible with water and is not acutely toxic to aquatic life at the limit of its solubility. The material floats on water and may form a film on water surfaces causing impaired oxygen transfer. 2EHN may emulsify with water.

3.4 Energetic Properties

2EHN is an organic nitrate. It undergoes a self-sustaining exothermic decomposition when it is heated above 100ºC. The product begins to decompose, giving off heat and decomposition gases; the heat energy is absorbed by the product promoting further and more rapid decomposition. Once established the decomposition reaction may be uncontrollable. Based on thermal decomposition data generated by ATC members and based on published data it is considered that fuel additive packages containing 15% or greater 2EHN may have the same energetic properties as the pure substance.

Section 4

First Aid Measures

Fuel additive packages are typically mixtures of several discrete components, each contributing to the overall hazard of the package. The potential hazards of the fuel additive package will therefore vary according to the nature and the concentration of the different chemistries present. Consequently, first aid advice may vary and the supplier's MSDS/SDS should always be consulted for detailed advice that is relevant to the fuel additive package. First aid advice specific to 2EHN present in fuel additive packages is, however, described below.

4.1 Inhalation

If the person is affected by inhaled vapours or combustion products, remove the person to fresh air at once. Provide respiratory support as needed. Get prompt medical attention.

4.2 Skin Contact

Immediately decontaminate contact area. Ensure shoes and/or clothing are free from material before reuse - discard if necessary. Get prompt medical attention.

4.3 Eye Contact

Although 2EHN has been shown not to be a primary eye irritant it is good practice to immediately decontaminate eyes with plenty of water following accidental exposure. Get prompt medical attention.

4.4 Ingestion

DO NOT induce vomiting, as aspiration of liquid product into the lungs can cause chemical pneumonitis. Get prompt medical attention.

4.5 Notes to Physicians

Treat exposure to a fuel additive package containing 2EHN as organic nitrate poisoning. Since 2EHN is a component of the product symptoms of vasodilatation may be present.

Section 5

Fire Fighting Measures

The flammable and thermal decomposition hazards presented by fuel additive packages containing 2EHN depends not only on the flash point and auto-ignition temperature but also on the heat of decomposition of the individual ingredients. Fuel additive packages typically contain flammable hydrocarbons and therefore these products are often classified as flammable (or at least combustible). The supplier's MSDS/SDS will contain specific fire-fighting measures and advice that are relevant to the fuel additive package.

Although the 2EHN component flash point may be well above recommended maximum transport, storage and handling temperatures for fuel additive packages (typically 40° - 60°C), fire and energetic decomposition hazard due to the presence of this substance is very high, due to its high heat of decomposition. Based on thermal decomposition data generated by members of ATC and based on published data **it is considered that fuel additive packages containing 15% or greater 2EHN may have the same energetic properties as the pure substance**. The supplier's MSDS/SDS will contain specific fire-fighting instructions for the fuel additive package, but it is recommended that the following additional precautions should be included in any risk management plan for fuel additive packages containing 15% or greater 2EHN.

Use chemical foam to extinguish the fire and large amounts of water spray preferably via a reliable fixed sprinkler/deluge system or by sufficient firewater monitors to cool containers and avoid catastrophic rupture of the storage vessel. Cool containers with flooding quantities of water until well after fire is out.

Alcohol-resistant foam directly injected into the storage vessel via a dedicated internal fixed system is the most effective extinguishing medium. Dry chemical powder and carbon dioxide are also effective with minor fires. Sand or earth might also be used to extinguish small fires.

Firewater capacity provided by firewater storage is to be sufficient to deliver firewater for long enough time to put fire under control (minimum of 6 hours at the maximum usage rate is recommended).

Protection of emergency personnel against smoke and combustion gases generated by large fires is vital.

5.1 Suitable extinguishing media

- For large fires: water spray, foam (alcohol resistant preferably).
- For small fires: dry chemical powder or CO_2.
- Do not use water jet.

5.2 Special fire fighting procedures

Removal of radiant heat from nearby fire is vital.

Radiant heat from surrounding fires can heat up tanks used to store fuel additive packages containing 2EHN. This could lead to bulk liquid phase decomposition with potential catastrophic effects. A credible scenario is that when a storage tank is involved in a fire, the upper tank surfaces in contact with the vapour will rapidly reach the auto-ignition temperature of the fuel additive package (for example, the auto-ignition temperature for pure 2EHN is 130°C) This will lead to an air-vapour explosion in the headspace of the tank, which could give rise to projectiles if its roof is not frangible. This hazard is well recognised for kerosine and gas-oil storage tanks where the auto-ignition temperatures are of the order of 250°C, more than 100°C higher than that of 2EHN.

Deluge water should be applied onto tank walls to keep the storage vessel cool. ***The calculated amount of water needed for effective removal of radiation heat coming from a fire in a nearby tank (15 m distant) is a minimum of 15 litre/minute/m² of exposed tank surface. Spray firewater at the required flow rate should be available for 6 or more hours.***

Cool containers exposed to flames with flooding quantities of water until well after the fire is out. Be aware of danger of container bursting under pressure followed by combustion of vapours. Fight any fire from a safe distance or protected locations. Do not approach containers suspected to be hot.

If tank, rail car or tank truck is involved in fire, ISOLATE the container and evacuate personnel to ensure safety.

Drums and IBCs should be immediately cooled by spraying firewater from a fixed deluge. Sealed drums of fuel additive packages containing 2EHN could rupture in

an intense fire after a short period of exposure (practical tests and theoretical examples indicate a time to rupture of 10 to 20 minutes for pure 2EHN, depending on conditions). Bursting drums will give rise to projectiles/ flying fragments and fireball formation, which will add to the severity of the incident.

5.3 Special protective equipment for fire-fighters

Exhaust gases from fire or products of decomposition are toxic (they contain oxides of nitrogen and combustion products). Therefore, it is recommended that fire-fighters are protected by wearing self-contained breathing apparatus (SCBA). Wear chemical protective clothing, however, such clothing may provide little or no thermal protection. Fire fighter's normal protective clothing will only provide limited chemical protection against exposure to 2EHN.

Section 6

Accidental Release Measures

Fuel additive packages are typically mixtures of several discrete components, each contributing to the overall hazard of the package. The potential hazards of the fuel additive package will therefore vary according to the nature and the concentration of the different chemistries present. Standard industrial practices for oil and hydrocarbon solvent spill control are generally applicable to fuel additive packages containing 2EHN. The supplier's MSDS/SDS should always be consulted for detailed advice that is relevant to the fuel additive package use but accidental release measures specific to 2EHN present in fuel additive packages are described below.

6.1 Personal precautions

When conducting clean up operations which might lead to accidental exposure by skin contact or inhalation, adequate personal protective equipment (PPE) should be worn. Ensure that the area is completely free from any residue of the spill before entering without protective equipment.

6.2 Environmental precautions

If possible, prevent spilled product from entering sewers and watercourses.

6.2.1 Small spillage

Suitable materials, such as commercial synthetic absorbent or sand can be used to absorb spills or leaks of fuel additive packages containing 2EHN.

Solid absorbent material should be shovelled up and placed in adequate sealed and properly labelled containers suitable for disposal. Additive packages containing 2EHN should not be allowed to enter the sewers. Do not flush out the product from contaminated areas.

6.2.2 Large spillage

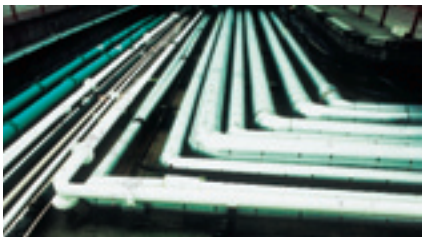
Contain spilled material within bunds or by creating temporary barriers. Use sand, earth, or other inert material to prevent the liquid entering drains, ditches or watercourses. Transfer the liquid by pumping into a dedicated, closed and properly labelled container. Ensure proper pumps are used and set up as recommended for the safe pumping of pure 2EHN (see section 7.3). Seek expert advice to dispose of large volumes of recovered product.

6.2.3.Spills onto water

Most fuel additive packages containing 2EHN will float. Spilled product can be confined by using floating barriers. Traditional oil spill control procedure should be applied as soon as possible to remove product from water. Local Authorities should be promptly notified about the potential adverse effect of 2EHN and other components contained in the fuel additive package on the aquatic environment since they can create a film on the surface of water and limit oxygen exchange.

Section 7

Handling and Storage



Fuel additive packages are typically mixtures of several discrete components, each contributing to the overall hazard of the package. The potential hazards of the fuel additive package will therefore vary according to the nature and the concentration of the different chemistries present. The supplier MSDS/SDS should be consulted for handling and storage advice concerning the specific package. It is, however, recommended that fuel additive packages containing 15% or greater 2EHN are handled and stored as though they were pure 2EHN, and additional measures for such products are described below.

7.1 Handling

7.1.1 Materials of construction

Suitable

Proper selection of materials of construction for 2EHN service is essential to ensure the integrity of the handling system and to maintain product quality.

Although stainless steel tanks are always preferred, fuel additive packages containing 2EHN may be stored in mild steel tanks provided they are kept free from water bottoms through regular maintenance. However, the use of mild steel containers with such products does require careful consideration because 2EHN can partition from the fuel additive package and hydrolyse slowly in the presence of water bottoms to form nitric acid. This in turn can increase the corrosion rate of mild steel.

Unsuitable

Galvanized steel, copper and copper bearing alloys are generally unsuitable for use with fuel additive packages containing 2EHN if water is present as the reaction of 2EHN with water leads to the corrosion of the alloys. Special care should be taken when selecting such items as pumps and valves to ensure that no copper alloys (e.g., brass or bronze) are used in bearings or other internal components that may come in contact with the product.

7.1.2 Elastomers and Gaskets

Fuel additive packages containing 2EHN are typically excellent solvents which can degrade the performance of some seals and gaskets. Therefore, careful selection is necessary. It is recommended that you contact your supplier for information.

7.2 Storage

7.2.1 Storage tanks

Many different sizes and types of tanks may be used to store fuel additive packages containing 2EHN and it is not possible to define one set of guidelines that covers every possibility. However, due to the thermal hazard characteristics associated with 2EHN it is crucial that heat can dissipate in the chosen storage vessel. The use of thermal ignition critical temperature calculations may help to define the safety precautions appropriate for any given tank.

In most respects, vertical tanks are the most practical overall solution. The relatively low auto-ignition temperature (130°C) of 2EHN can lead to an air-vapour explosion in the headspace of vessels, which can rupture, spilling the contents. Vapour-air explosions release less energy per unit volume than those resulting from self-reaction of the liquid and peak blast force is a key design criterion. Vertical tanks can be fitted with a frangible roof to minimize damage in case of a pressure blow-out. API 650 is a widely used standard that can be used as reference for specifying such tanks. Vertical tanks are also easier to configure with water deluge systems.

If horizontal tanks are used for the storage of fuel additives containing 2EHN they have no ‘roof’ so the fitting of a frangible roof is not an option. If the contents are heated above 100°C, then there is a risk that the tank will fail at the dished ends and form a “missile” with potentially catastrophic effects. Safety principles should be strictly applied to prevent heating of such additives in horizontal tanks.

A fire in the storage area will heat the storage tanks. A fixed deluge system to supply cooling water in event of fire must be present to minimize this risk. API 650 standard indicates that a system that delivers a cooling-water flow rate of at least 15 litre/minute/m^2 of storage tank surface area can achieve effective cooling. If this volume of water is not continuously available for cooling purposes, additional non-insulating fire cladding of the tank walls could be considered within the context of the overall risk assessment of the storage facility.

Risk of tanks bursting under pressure should be minimized - See also Sections 7.2.2 and 7.2.3.

7.2.2 Heat protection

The principle here is to protect the product from heat.

For fuel additives containing at least 15% 2EHN a deluge system provides the best protection against product overheating. No heating system of any kind should be installed and existing heating systems must be permanently disabled. When laying out the route for new pipe work to carry fuel additive packages containing 2EHN, the designer should avoid sources of heat and potential fire. When using existing pipe work installations, the designer should ensure that heated pipes are not used for fuel additive packages containing 2EHN.

As a general principle, locating storage tanks in an open area away from inhabited buildings is recommended. The site should be remote from possible fire hazards to minimize their exposure to external heat and fire impingement if fire breaks out. The extent of this separation is a local decision to be determined by the site risk assessment. For example, the NFPA 30 standard may be used to help determine the appropriate distance from other storage tanks and equipment to maintain protection in case of fire.

Firewalls between the tanks will improve thermal protection. If sufficient space is not available for firewalls, then non-insulating tank-wall fire cladding may provide additional protection. Screening walls and non-insulating fire cladding may be used in combination to achieve acceptable protection. The better the protection, the longer the time the stored fuel additive packages containing 2EHN will endure external heating and the lower the risk of thermal decomposition within the storage system. Instrumented fire and heat detection systems should be installed.

7.2.3 Venting

Bulk storage vessels should preferably be vented directly into the atmosphere far from ignition sources if local regulations permit. Conservation vents with frangible roof seams are also acceptable. For smaller equipment, standard engineering practices for design of emergency discharge should be followed.

Tanks containing fuel additive packages containing 2EHN should preferably be at atmospheric pressure. The vent outlet is to be positioned in a safe area sufficiently high and far from ignition sources.

7.2.4 Containment wall or Bunding

To minimize the consequences of a spill and leakage into the environment, a containment wall (bund) should surround tanks with a minimum capacity to handle tank contents and deluge water.

7.2.5 Drum storage

Ensure good ventilation during drumming/ de-drumming. Filled drums should be stored far from heat sources and other flammable products and protected by firewater. Special care should be taken when opening drums, which may be pressurized.

7.3 Operations

7.3.1 Product sampling

Product sampling is a potential source of personnel exposure to 2EHN. Design and procedures should be developed to minimize exposure of personnel and the environment to fuel additives containing 2EHN.

7.3.2 Product handling - loading, unloading, pumping

Loading

The use of a dedicated loading arm is preferred. If a multi-compartment tank wagon is loaded, ensure fuel additive packages containing 2EHN are not shipped adjacent to heated cargoes. Ensure proper electrical grounding and electrical continuity on all installations to control static electricity.

Unloading

Use a dedicated hose. Control static electricity. Avoid manifolds to prevent accidental ingress of fuel additive packages containing 2EHN into heated lines.

Pumping

Since 2EHN is a self-reactive substance it can decompose in the absence of air in the bulk liquid phase if heated. This occurs most commonly under pressure in a blocked or dead headed pump, or other sealed system, and can lead to violent bursting of the equipment. To avoid this situation developing it is recommended that the equipment does not have the potential to heat the product. The pump

manufacturer should always be consulted to ensure that any equipment meets these specifications. Pumped transfer of fuel additive packages containing 2EHN should always be done under controlled conditions and all transfer valves must be open before pumps are started. It is inadvisable and dangerous to pump against a closed outlet because this may heat the product within the pump, depending on the type of pump in use.

Pneumatically-powered diaphragm pumps provide an inherently safe and reliable means of pumping fuel additive packages containing 2EHN.

Centrifugal pumps are not as inherently safe as pneumatic diaphragm pumps and if used extra control systems are required. Gear pumps and other positive displacement systems can heat 2EHN rapidly when the pump outlet is closed or blocked. Consequently, their use is not recommended for fuel additives containing 15% or greater 2EHN.

Regardless of the pump design, it is recommended that safety pump trip controls and instrumentation must be fitted with:

- A temperature trip set to stop the pump at a product temperature of 50-60°C.
- In exceptional circumstances, specific operations may require a higher temperature trip set up to a maximum of 75°C, subject to detailed expert risk assessment in conjunction with your fuel additive supplier.
- A pressure switch to stop the pump if the outlet is blocked or closed and/or
- A low flow switch to stop the pump if the outlet is blocked or closed.

To prevent the risk of heating the product closed circuit pumping, including that through pressure relief valves when the pump outlet is closed or blocked, must be avoided. It is worth remembering that the majority of incidents involving 2EHN have been due to overheating of pumps and resulting bursting of the equipment. Careful consideration of the siting of pumps needs to be made and the consequences of pump failure needs to be fully assessed to minimize the risk of an incident occurring.

7.3.3 Tank to tank transfer

Tank to tank transfer of fuel additive packages containing 2EHN can be safely carried out using nitrogen or air padding, by using a pneumatic driven pumping system or pumps as described above.

7.3.4 Piping / Lines / Hoses

Use non-insulated Mild Steel or Stainless Steel piping.

Any steam or electrical tracing must be physically disconnected.

Wherever possible, dedicated lines for fuel additive packages containing 2EHN are preferred to avoid safety/environmental problems. The installation of a pressure release valve is recommended. Experimental fire testing of gantry-type pipe-work filled with an additive containing approximately 70% 2EHN showed that a pressure relief valve set at 10 bar was sufficient to relieve pressure caused by the self-heating accelerating decomposition of 2EHN. If fitted, the pressure relief valve should discharge to a safe location.

7.3.5 Valves

Stainless Steel full-bore ball valves are preferable. Traditional ball, gate and butterfly valves may also be used. Stainless steel, cast iron and cast steel are all suitable materials. Copper, zinc and its alloys, aluminium and most plastics are inadequate or incompatible materials.

7.3.6 Equipment clean-up

Inadequate cleaning of equipment or pipe work introduces the risk of environmental contamination and potential for decomposition of 2EHN residues. A specific procedure should be developed by skilled personnel, which recognises the health and environmental hazards and the temperature limits to ensure that cleaning operations are conducted in effective and safe manner.

Section 8

Exposure Controls and Personal Protection

Fuel additive packages are typically mixtures of several discrete components, each contributing to the overall hazard of the package. The potential hazards of the fuel additive package will therefore vary according to the nature and the concentration of the different chemistries present. Consequently, the mechanical controls and personal protective equipment required to protect the user against exposure will vary depending on the type and amount of the different chemistries present. The supplier's MSDS/SDS should always be consulted for detailed advice that is relevant to the fuel additive package supplied. However, mechanical controls and personal protective equipment specific to 2EHN present in fuel additive packages is described below.

8.1 Exposure limit values

2EHN manufacturers and suppliers have recommended an internal exposure limit of 1 ppm based on an 8hr time weighted average (TWA). Due to the potential for temporary harmful effects of overexposure, it is suggested that 1 ppm should also be adopted as the reference standard for short term exposures averaged over 15 minutes (STEL). This exposure guideline is intended to set a level which does not subject an employee to over-exposure during normal product handling. However, it is not a regulated limit that has been established by a governmental or other agency.

8.2 Exposure controls

If an operation creates the potential for employee exposure by inhalation or skin contact, accepted engineering or administrative controls should be the first choices minimising exposure. When effective engineering or administrative controls are not feasible, or when they are being implemented or evaluated, appropriate respiratory and skin protection should be used to control employee exposure to fuel additives containing 2EHN.

8.3 Personal Protective Equipment

8.3.1 Respiratory protection

2EHN has a very persistent odour with a low odour threshold. Respiratory protection is recommended for open systems or where concentration of 2EHN in the working environment may exceed the recommended exposure guideline of 1 ppm (TWA or STEL). The respirator chosen should be appropriate for the exposure potential, level of exposure and working conditions. Respirator suppliers are best placed to offer advice concerning the suitability of their product to protect the wearer against exposure to 2EHN by inhalation.

8.3.2 Hand protection

When skin contact is possible, appropriate chemical resistant gloves (neoprene or nitrile rubber) should be worn covering at least to the wrist (depending on the extent of immersion). Glove suppliers are best placed to offer advice concerning the suitability of their product to protect the wearer against exposure to 2EHN by skin contact.

8.3.3 Eye protection

Eye protection should be chosen based on the exposure potential and working conditions. There are no additional eye protective measures required due to the presence of 2EHN in the fuel additive packages.

8.3.4 Skin protection

When skin contact is likely, appropriate skin protection should be used. Leather clothing can be hazardous when they have become contaminated with 2EHN. Leather can absorb 2EHN and maintain a continuous low level exposure over a prolonged period of time.
Thus, leather clothing and other items should not be specified as protective clothing for handling fuel additive packages containing 2EHN, and should be removed and destroyed promptly if they become contaminated.

Section 9

Physical and Chemical Properties

Fuel additive packages are typically mixtures of several discrete components, each contributing to the overall hazard of the package. The physical and chemical properties of fuel additive packages containing 2EHN will therefore vary according to the nature and the concentration of the different chemistries present. The supplier's MSDS/SDS will contain this information for the specific fuel additive package supplied. For comparative purposes, however, typical physical properties of pure 2EHN are given below.

Physical Properties

Appearance	Colourless to pale yellow liquid
Odour	Fruity, pungent, ester, characteristic
Molecular weight	175.23
Flash point	>70°C (closed cup)
Freezing point	<-45°C
Boiling point	>100°C (decomposes)
Vapour pressure	27 Pa @ 20°C
Vapour pressure	40-53 Pa @ 40°C
Vapour pressure	1.33 kPa @ 82°C
Density	0.96 g/ml @ 20°C
Kinematic Viscosity	1.8 cSt @ 20°C
Solubility in water	12.6 mg/L @ 20°C

Heat of vaporization	368 kJ/kg
Heat of decomposition	2100 J/g
Dielectric constant	9.04 @ 21-23°C
Lower Explosive Limit	0.25% v/v in air (literature value – source unknown)
Auto / Self ignition temperature	130°C (decomposes)
Thermal Ignition Critical Temperature - Self-accelerating decomposition temperature	Function of time and geometry of the container (see appendix 2 for explanation of Thermal Ignition Critical Temperature).
Log Pow	3.74 (calculated) - 4.14, (iso-octyl nitrate)
Decomposition temperature	>100°C

Section 10

Stability and Reactivity

Fuel additive packages are typically mixtures of several discrete components, each contributing to the overall hazard of the package. Consequently, the stability and reactivity of the specific product will vary depending on the type and amount of the different chemistries present. The supplier's MSDS/SDS should always be consulted for detailed advice that is relevant to the fuel additive package supplied. However, the stability and reactivity of fuel additive packages containing 15% or greater 2EHN should be considered to be the same as pure 2EHN and relevant considerations are described below:

2EHN is stable at ambient temperatures. However it has a low auto-ignition temperature and will decompose when heated above 100°C. This temperature is significantly lower than the auto-ignition temperature of common hydrocarbon fuels (see table 1 opposite).

Table 1: Comparative Auto-ignition Temperatures

	Auto-ignition Temperature °C
2-Ethylhexyl Nitrate	130
Diesel Fuel / Fuel Oil	220-300
Gasoline: 100 RON Octane	456
Avgas: 100-130 RON Octane	440
115-145 RON Octane	471

The auto-ignition temperatures (AIT) of various dilutions of 2EHN in kerosene are shown in Table 2 below. These data show that 2EHN has a significant effect of lowering the auto-ignition temperature down to low concentrations.

Table 2: Auto-ignition Temperatures

Vol.% of 2EHN	Vol.% Kerosene	AIT °C	Flash (TCC) °C
100	0	130	70
95	5	180	—
90	10	175	—
85	15	180	—
75	25	185	71.1
50	50	185	65
25	75	200	61.7
10	90	210	60.5
0	100	250	60.5

Fuel additive packages containing 2EHN are normally stable at ambient temperatures. However the above data and other thermal decomposition data generated by members of ATC shows that a thermal hazard can remain even at relatively low levels of 2EHN when heated above 100°C.

10.1 Conditions to avoid

Due to the presence of 2EHN it is recommended to avoid all contact with sources of heat, flames, sparks or any other source of ignition. Vapours may be explosive. Avoid overheating of containers. Containers may violently rupture in heat of fire.

10.2 Materials to avoid

It is recommended to avoid contamination with acids, alkalis, reducing and oxidising agents, and phosphorus. Alkyl nitrates typically react violently with strong mineral acids, tin (IV) chloride, boron trifluoride, and other Lewis acids after an induction period of up to several hours to produce a vigorous evolution of gas such as oxides of nitrogen. Traces of nitrogen oxides can promote decomposition of alkyl nitrates. This can lead to container rupture on heating or pressure build up on prolonged storage at ambient temperatures. Transition metal oxides or their chelates also greatly accelerate the decomposition rate.

10.3 Hazardous decomposition products

Combustion or thermal decomposition products of 2EHN are oxides of carbon and nitrogen and other constituents.

Section 11

Toxicological Information

Fuel additive packages are typically mixtures of several discrete components, each contributing to the overall hazard of the package. The potential hazards to human health of the fuel additive package and the overall hazard classification concerning health end points will therefore vary according to the nature and the concentration of the different chemistries present. The supplier MSDS/SDS should be consulted for toxicological effects associated with the specific package and/or individual components. Toxicological effects that can be attributable to 2EHN present in fuel additive packages are, however, described on the next page.

11.1 Acute Health Effects

11.1.1 Oral (Ingestion)

The oral toxicity attributed to 2EHN when tested in animals is low.

LD50 is >5000 mg/kg (rat) and therefore is not classified as harmful or toxic if swallowed.

Fuel additive packages containing 2EHN are, however, likely to present an aspiration hazard.

11.1.2 Inhalation

Exposure to 2EHN through inhalation can result in vasodilatation (reduced blood pressure, and other cardiovascular effects to produce such symptoms as throbbing headache, flushing, light-headedness, transient dizziness or weakness, heart palpitations, nausea, fatigue, confusion and possible loss of consciousness).

11.1.3 Dermal (Skin)

Exposure to 2EHN through skin contact can result in vasodilatation (symptoms as described in 11.1.2).

11.2 Corrosivity / Irritation

11.2.1 Skin

2EHN is not a primary skin irritant based on experimental data and therefore should not contribute to any potential risk of skin irritation associated with the fuel additive package. Prolonged skin contact may however produce temporary discomfort.

11.2.2 Eye

2EHN is not a primary eye irritant based on experimental data and therefore should not contribute to any potential risk of eye irritation associated with the fuel additive package. Eye contact may however produce temporary discomfort.

11.3 Sensitisation

2EHN has been shown to not cause skin sensitization based on experimental data. Furthermore, there have been no reports of human skin sensitization from occupational exposure to this substance. 2EHN should not contribute to any potential risk of skin sensitization associated with the fuel additive package

11.4 Chronic Health Effects

No significant chronic, mutagenic, carcinogenic, reproductive or developmental effects are known for 2EHN.

Section 12

Ecological Information

Fuel additive packages are typically mixtures of several discrete components, each contributing to the overall hazard of the package. The potential environmental hazard of the fuel additive package and the overall hazard classification concerning environmental end points will therefore vary according to the nature and the concentration of the different chemistries present. The supplier MSDS/SDS should be consulted for potential adverse effects associated with the specific package and/or individual components. Environmental effects that can be attributable to 2EHN present in fuel additive packages are, however, described below.

12.1 Ecotoxicity

2EHN is not classified as Dangerous for the Environment according to European Union hazard criteria because there were no adverse effects in fish, invertebrates (*Daphnia*) or algae at the limit of its solubility. It is however classified as a marine pollutant by the International Maritime Organisation.

12.2 Mobility

The octanol/water partition coefficient of 2EHN predicts moderate mobility/moderate affinity for soil or sediment.

12.3 Persistence and degradability

2EHN shows no evidence of biodegradability in the aqueous environment.

12.4 Bioaccumulation potential

2EHN is completely miscible with fat and the calculated Octanol-Water Partition Co-efficient (log_{10}Pow >3) indicates that this substance has potential for bioaccumulation.

12.5 Other adverse effects

Fuel additive packages containing 15% or greater 2EHN may form a film on the water surface affecting oxygen transfer.

Section 13

Disposal Information

Fuel additive packages are typically mixtures of several discrete components. Permitted methods of disposal will therefore vary according to the nature and the concentration of the different chemistries present. The supplier MSDS/SDS should be consulted for disposal instructions concerning the specific product supplied. However, disposal instructions that are relevant to 2EHN present in fuel additive packages are described below.

The product should be recovered whenever possible. Fuel additive packages containing 2EHN are not suitable for landfill or treatment by biological processes. Incineration in approved onsite or offsite facilities equipped with flue gas post-combustion, wet scrubbing and de-dusting systems is the preferred disposal practice. Provided that 2EHN is not confined, there should be no risk of violent decomposition if product is disposed of in this manner. Thermal decomposition and fire may also occur with wastes containing 2EHN if overheating or contact with reactive materials occurs.

Section 14

Transport Information

Fuel additive packages are typically mixtures of several discrete components, each contributing to the overall transport hazard of the package. The potential hazards of the fuel additive package and its transport classification will therefore vary according to the nature and the concentration of the different chemistries present. The supplier's MSDS/SDS should always be consulted for detailed transport classification advice concerning the fuel additive package supplied.

2EHN does not meet the criteria for Class 9 but it is classified as an environmental hazard (marine pollutant) according to the IMO's IMDG and BCH codes. This classification was based on data submitted on a blend of alkyl (C7-C9) nitrates, predominately C8, which are no longer marketed. Since 2EHN does not meet the criteria of any of the other transport classes, all suppliers of 2EHN currently classify this substance as Class 9 hazard for transport. In view of the energetic properties of 2EHN, there is a proposal to obtain a specific entry for 2EHN in the UN orange book to more accurately reflect its hazardous properties, and if adopted this may need to be taken into account in the future when classifying fuel additive packages containing 2EHN for transport hazard.

Section 15

Regulatory Information

Fuel additives packages are typically mixtures of several discrete components, each contributing to the overall supply hazard of the package. The potential hazards of the fuel additive package and its classification for supply will therefore vary according to the nature and the concentration of the different chemistries present. The supplier's MSDS/SDS should always be consulted for detailed classification and labelling advice concerning the fuel additive package supplied. However, classification and labelling that can be attributable to 2EHN present in fuel additive packages is described below.

15.1 EU classification and labelling

2EHN is classified as Harmful by inhalation and skin contact (R20/21). Based on the Dangerous Preparations Directive limits for substances classified as R20/21 [(1)], fuel additive packages containing 25% or greater 2EHN by mass would be expected to be classified as Harmful and have the Risk Phrase R20/21 assigned.

In addition, data generated by ATC member companies suggest that fuel additive packages have a risk of significant energetic decomposition when they contain 2EHN at 15% or greater and it would therefore be prudent to assign the Risk Phrase R44 to such products.

Section 16

Other Information

16.1 Training

A comprehensive and ongoing training programme in the handling, use, storage and disposal of fuel additive packages containing 2EHN is of significant value to all personnel. Contact your supplier for assistance if needed.

16.2 Emergency Procedures for 2EHN

Written emergency procedures should be in place when handling fuel additive packages containing 2EHN. This procedure should include fire and decomposition scenario.

(1) Annex II Part B Table 1; Directive 1999/45/EC of the European Parliament and of the Council of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations.

Appendix 1

Responsible Care®

Many of the member companies of ATC have a long standing policy to ensure that their operations do not have an adverse impact on the community or the Environment. Responsible Care®, a continuing effort by the chemical industry to improve the responsible management of chemicals, is one way member companies of ATC are meeting this commitment.

What is Responsible Care®?

Responsible Care® is the Chemical Industry's commitment to continuous improvement in all aspects of environmental, safety and health protection. Although voluntary, all member companies throughout the world have committed to the principle of continuous improvement through self-evaluation and regular assessment with key indicators of performance being published on an annual basis. Responsible Care® continues to strengthen its commitments and enhance the public credibility of the industry. New program enhancements adopted by the American Chemistry Council as a condition of membership include:

1) A Responsible Care® Management System;
2) An independent third party certification of the management system to ensure appropriate actions are taken to improve performance;
3) Tracking and publicly reporting performance based on economic, environmental, health and safety, societal and product related metrics;
4) A Security Code that helps protect people, property, products, processes, information and information systems by enhancing security throughout the chemical industry value chain.

Appendix 2

Explanation of thermal ignition critical temperature

The thermal ignition critical temperature (T_C) is the lowest surface temperature at which an energetic material can go into runaway self-heating reaction. However, when this temperature is reached, self-heating does not immediately ensue.

After a sample reaches thermal ignition critical temperature there is a finite amount of time before self-heating occurs.

One concern with energetic materials like 2EHN (i.e. those that release large amounts of heat when they decompose) is their potential to initiate a runaway self-heating cycle. At the temperature where the rate of 2EHN decomposition exceeds the rate at which the generated heat can be dissipated to the surroundings, the product begins to self-heat. The surface-to-volume ratio of a product container is an important factor in determining how fast heat can be dissipated: the smaller the surface-to-volume ratio of the container, the lower the temperature at which runaway self-heating begins.

When the quantity of energetic material is very large, such as found in very large storage tanks, self-heating and thermal runaway could become a problem at very high constant ambient temperatures.

Various scenarios have been modelled using the Frank-Kamenetskii equation, which postulates the heating to runaway reaction of an unstirred, insulated energetic substance. The ambient temperature and the size or shape of the reactant system are important. There is a range of data available on 2EHN from different sources, however, small variations in the assumptions can have a very large effect on the results. If the maximum long-term storage temperature is kept below 40°C then no problems with self-heating and thermal runaway are envisaged.

Glossary

Term	Where	Definition
Product stewardship	Front page	Product-centred approach to environmental, health and safety protection. It calls on those in the product life cycle - manufacturers, retailers, users, and disposers - to share responsibility for reducing the environmental, safety and health impacts of products.
Cetane number	Section 1.1	The performance rating of a diesel fuel, corresponding to the percentage of cetane in a cetane-methylnaphthalene mixture with the same ignition performance.
Cetane number improver	Section 1.1	A chemical compound, typically 2-Ethylhexyl nitrate (2EHN), used to reduce combustion noise and smoke. Also known as Diesel Ignition Improvers.
ATC	Section 1.2	Additives Technical Committee. This is also known as the Technical Committee of Petroleum Additive Manufacturers in Europe. ATC provides a forum for additive companies to meet and discuss developments of a technical and/or statutory nature concerning the application of additives in fuels, lubricants and other petroleum products.
CEFIC	Section 1.2	Conseil Européen des Fédérations de l'industrie Chimique (or the European Chemical Industry Council). This is the largest association of chemical companies in Europe and represents directly or indirectly, about 40,000 large, medium and small chemical companies.
Explosive substance	Section 1.2	A compound or mixture susceptible (by heat, shock, friction or other impulse) to a rapid ***chemical*** reaction, ***decomposition*** or ***combustion*** with the rapid generation of heat and gases with a combined volume much larger than the original substance.
Energetic properties	Sections 1.2 / 3.4	The substance can possess or exert energy.
IUPAC name	Section 2	A chemical name assigned using nomenclature rules recommended by the International Union of Pure and Applied Chemistry.
EINECS name	Section 2	A chemical name as it appears on the European Inventory for Existing Commercial (Chemical) Substances.
CAS number	Section 2	The unique identification number for a chemical substance listed on the Chemical Abstracts Service.
EINECS number	Section 2	The unique identification number for a chemical substance listed on the European Inventory for Existing Commercial (Chemical) Substances.
Energetic substance	Section 3.1	Substances which because of their chemical structure are capable of undergoing rapid exothermic decomposition with release of energy.
Vasodilatation	Section 3.1	Dilation of blood vessels possibly leading to reduced blood pressure and other cardiovascular effects to produce such symptoms as throbbing headache, confusion and possible loss of consciousness.
Aspiration hazard	Section 3.1	A substance that poses a threat to the body if inhaled.

Term	Where	Definition
Acute health effect	Section 3.2.1	Adverse effects resulting from a single exposure to a substance.
Chronic health effects	Section 3.2.2	Hazards such as cancer, reproductive or developmental damage, neurological or other organ damage to animals or humans related to repeated or long term exposure.
Environmental hazards	Section 3.3	Intrinsic properties of a chemical substance or mixture that present a danger to the environment, and in particular to aquatic organisms.
Flash point	Section 5	Lowest temperature at which a flame will propagate through the vapour of a combustible material to the liquid surface. It is determined by the vapour pressure of the liquid, since only when a sufficiently high vapour concentration is reached, can it support combustion. Two general methods are called closed-cup and open-cup.
Closed cup	Section 5	The closed-cup method prevents vapours from escaping and therefore usually results in a flash point that is a few degrees lower than in an open cup. Because the two methods give different results, one must always list the testing method when listing the flash point. Example: 110ºC (closed cup).
IBC /IBCs	Section 5.3	Intermediate Bulk Container. For liquids this is normally a rigid or flexible portable package with a capacity of less than $3m^3$ that is designed for mechanical handling.
Commercial synthetic absorbent.	Section 6.2.1	A material having capacity or tendency to absorb another substance.
Floating barriers	Section 6.2.3	A device designed to float on the surface of water, specifically to contain and/or absorb floating oily substances i.e. “oil boom”.
Thermal ignition critical temperature	Section 7.2.1	The temperature at or above which heat is generated faster than it can be dissipated. Reaching the critical temperature can be expected to result in a self-accelerating reaction. See appendix 2 for further details.
Frangible roof tank	Section 7.2.1	A tank with a roof to shell connection which is designed to fail before the bottom to shell joint. This type of failure prevents loss of tank contents and feeding the fire.
API 650	Section 7.2.1	A standard for welded steel tanks for oil storage. Published by the American Petroleum Institute. This standard is designed to provide the petroleum industry with tanks of adequate safety and reasonable economy for use in the storage of petroleum, petroleum products, and other liquid products commonly handled and stored by the various branches of the petroleum industry. It is intended to help purchasers and manufacturers in ordering, fabricating, and erecting tanks. Standard 650, Tenth Edition, covers material, design, fabrication, erection, and testing requirements for vertical, cylindrical, aboveground, closed- and open-top, welded steel storage tanks in various capacities for internal pressures approximating atmospheric pressure, but a higher internal pressure is permitted when additional requirements are met. This standard applies only to tanks whose entire bottom is uniformly supported; and to tanks in non-refrigerated service, that have a maximum operating temperature of 93.3ºC (200ºF).
Non insulated fire cladding/non-insulating tank-wall fire cladding	Section 7.2.1	A protective layer fixed to the outside of a structure, in this case a tank wall.
NFPA 30	Section 7.2.2	Flammable and Combustible Liquids Code published by the National Fire Protection Association, USA. Applies to all flammable and combustible liquids except those that are solid at 37.8ºC (100ºF) or above. Covers tank storage, piping, valves and fittings, container storage, industrial plants, bulk plants, service stations and processing plants.

Term	Where	Definition
Firewalls	Section 7.2.3	A wall of incombustible construction which subdivides a building or separates buildings to restrict the spread of fire and which starts at the foundation and extends continuously through all stories to and above the roof, except where the roof is of fireproof or fire-resistive construction and the wall is carried up tightly against the underside of the roof slab.
Conservation vents with frangible roof seams Frangible roof seams	Section 7.2.3	A device designed to limit the breathing of a storage tank, through use of a liquid or mechanical seal. Often used in conjunction with inert gas in order to preclude introduction of air into a storage tank. - a vertical tank roof seam specially designed to split open should the tank be subjected to pressures above its design rating.
Static electricity	Section 7.3.2	Electrical charge generated by friction between two materials or substances.
Exposure limit values: 8hr time weighted average (TWA) and Short-term exposure limit (STEL).	Section 8.1	The 8hr TWA Exposure Limit Value is the concentration to which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse health effects. A STEL is the concentration to which it is believed that workers can be exposed continuously for a short period of time and it should not occur more than 4 times per day.
Self-Accelerating Decomposition Temperature (SADT)	Section 9	Used in the classification of substances for transport. The lowest temperature at which a self-accelerating decomposition (runaway) may occur in the package as used in transport. The SADT varies with the mass of substance and the shape of the package. It is used to determine safe temperatures during transport and can offer a guide to instability in storage and use.
Log Pow	Section 9	Pow is the partition coefficient (P) of a substance dissolved in a two-phase system consisting of n-octanol and water. The concentration (C) of a substance is measured during each phase after achieving equilibrium and is represented as a quotient of the two concentrations *C octanol/C wate*r. The partition coefficient is usually presented in the form of its logarithm to the base ten. It may also be referred as a *Log Ko*w, or *Log* P.
Lewis acids	Section 10.2	A chemical species that can accept a pair of electrons and form a covalent bond. Examples include boron trifluoride, sulphur dioxide, sulphur trioxide and phosphorus pentachloride.
Transition metal oxides or their chelates Chelates:	Section 10.2	Compounds comprising a metal with an unfilled "*d*" sublevel and oxygen. Examples are iron oxide, zinc oxide, copper oxide and manganese oxide. - Compounds comprising a metal with an unfilled "*d*" sublevel and an organic chemical with two or more functional groups. Such chelates have a ring structure.
LD50 (oral, dermal)	Section 11.1.1 Section 11.1.3	The single dose that will kill 50% of the test animals by any route other than inhalation such as by ingestion or skin contact.
LC50	Section 12.1	The concentration in water that will kill 50% of the test animals when exposed over a specific time period, usually 96 hours.
EC50	Section 12.1	Median Effective Concentration (required to induce a 50% effect)