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Chemical Category	NITROETHANE		

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ANGUS

January 13, 1986



INIT 07/26/94

Mr. Louis Borghi
Dynamac Corporation
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852



84940000219

Dear Mr. Borghi:

As discussed in our telephone conversation, ANGUS Chemical Company will supply detailed information on nitroethane as soon as it is determined what information is CBI and, in the case of our inhalation study, a written report becomes available. In the meantime, I can answer some of your questions in a general manner.

Production Volume and Process Data

The four nitroparaffins, Nitromethane (NM), Nitroethane (NE), 1-Nitropropane (1-NP), and 2-Nitropropane (2-NP), are all produced by the nitration of propane in gaseous phase. The resulting mixture of nitroparaffins is then separated and marketed as the individual substances. It must be emphasized that these four substances are obtained at a fixed ratio. Only very minor variations in the ratio of products can be obtained by altering the conditions of reaction. Our overall capacity is approximately 90 million pounds. NE capacity is on the order of 4-8 million pounds.

Use Information

The largest portion of NE is used as a chemical intermediate, in particular for the production of the drug Aldomet. Some NE is used as part of the stabilizer for chlorinated solvents (less than 0.5% by wt. is used). Only about 100,000 pounds is used in specialized coatings applications.

Regulations of nitropropane would, in general, have a detrimental effect on the NE market:

1. We cannot make NE without obtaining several times as much nitropropane. If the nitropropane cannot be sold, NE prices would have to be raised considerably higher than its current price of approximately \$2.60 per pound.

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Page 2
Mr. Louis Borghi
January 13, 1986

2. Because of the difference in price, approximately \$2.60 for NE vs. approximately \$.60 for nitropropane, there is no way that NE could replace nitropropane in its major end-use, i.e. coatings.
3. From the appearance of the first NIOSH Intelligence Bulletin to date, our market for 2-NP has shrunk from approximately 20 million pounds to about 5 million pounds. Only the development of derivatives of 2-NP, as a place to use excess 2-NP production, has enabled us to keep our plant running smoothly.

Unpublished Toxicity Data

I enclose a copy of TDS No. 21 on NE. On page 6 is a summary of toxicity data. Most of the inhalation data is quoted from, "Experimental Toxicological Study of Some Nitroparaffins, III. Nitroethane," J. Dequidt, et al., Bull. Soc. Pharm. Lille, 1972, 83-87, (we have an English translation).

Other than the data summarized in TDS 21, we do have a recently completed lifetime inhalation study in rats. Exposure levels were 100 ppm and 200 ppm. Verbal reports are that no oncogenic effects were observed in any of the test animals. We are now awaiting a written report on this study. A copy of our Material Safety Data Sheet is enclosed.

Occupational Exposure Data

We have no information on exposures in the workplaces of users of NE. Levels in our manufacturing plant generally are less than 1 ppm for all four nitroparaffins. Our epidemiology study on 2-NP actually is valid for nitroethane because the workers are exposed to all four nitroparaffins.

Environmental Data

Little data is available. However, there are several literature references in which NE is shown to be assimilated by microorganisms. In fact, one study used NE as the sole source of nitrogen for the growth of a wide range

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Page 3
Mr. Louis Borghi
January 13, 1986

of microbe cultures. ANGUS Chemical Company has been concerned by the unavailability of definitive studies. Accordingly, it has begun a test program to obtain such data for most of its major products. I believe that the first tests in this series are now underway (NM is the first in this series).

I hope the above information is useful to your efforts. Please let me know when and if further information is desired.

Very truly yours,

A handwritten signature in cursive script that reads "A. Bollmeier Jr." The signature is written in dark ink and is positioned above the typed name.

Allen F. Bollmeier, Jr.
Manager, Technical Communications

nd

Enclosures

cc: Mr. Robert F. Purcell

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MATERIAL SAFETY DATA SHEET



ANGUS Chemical Company
 2211 Sanders Road
 Northbrook, IL 60062
 (312) 498-6700

24-Hour Emergency Telephone
 (318)665-4451

HMIS Hazard Rating
 Health 1
 Flammability 3
 Reactivity 1

CHEMICAL NAME Nitroethane	TRADE NAME NE
CHEMICAL FAMILY Nitroalkane	FORMULA CH ₃ CH ₂ NO ₂

	INGREDIENT	% BY WT.	CAS REG. NO.
HAZARDOUS INGREDIENTS	Nitroethane	~96.0-98.0	79-24-3
	2-Nitropropane	~1.5-3.0	79-46-9

OTHER INGREDIENTS	INGREDIENT	% BY WT.	CAS REG. NO.

PHYSICAL DATA	BOILING/MEETING POINT (°C)	114	SPECIFIC GRAVITY 20/20°C	1.052
	VAPOR PRESSURE		PERCENT VOLATILE	
	MM Hg AT 20 °C	15.6		100
	VAPOR DENSITY (AIR = 1)	2.58	EVAPORATION RATE n-BUTYL ACETATE = 100	121
	SOLUBILITY IN WATER by vol. at 20°C	4.5		
	APPEARANCE AND ODOR	Colorless liquid, characteristic odor.		

FIRE AND EXPLOSION HAZARD DATA	FLASH POINT 87°F TCC	FLAMMABLE LIMITS	LEL % 4.0	UEL % unknown
	EXTINGUISHING MEDIA Water spray, foam, CO ₂ and only those dry chemical extinguishers rated: triclass ABC.			
	SPECIAL FIRE FIGHTING PROCEDURES Wet down tanks and containers to prevent rupture. Avoid breathing vapors.			
	UNUSUAL FIRE AND EXPLOSION HAZARDS Use <u>only</u> those dry chemical extinguishers rated for use on Class A, B, and C fires. Do not use bicarbonate-based dry chemical extinguishers in fighting fires. Dry salts formed with strong alkalis may be ignitable; keep them away from sparks and flame.			

The information, data, and recommendations contained herein are believed to be accurate. However, we make no warranty of any kind whatsoever with respect thereto and disclaim all liability from reliance thereon.

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REACTIVITY DATA	STABLE <input checked="" type="checkbox"/> UNSTABLE <input type="checkbox"/>	CONDITIONS TO AVOID Extreme shock under heavy confinement at high temperature.
	INCOMPATIBILITY (MATERIALS TO AVOID) Lead, copper or their alloys; strong alkali.	
	HAZARDOUS DECOMPOSITION PRODUCTS Oxides of carbon and nitrogen.	
	HAZARDOUS POLYMERIZATION MAY OCCUR <input type="checkbox"/>	CONDITIONS TO AVOID HAZARDOUS POLYMERIZATION WILL NOT OCCUR <input checked="" type="checkbox"/>

SPILL OR LEAK PROCEDURES	STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED Remove all ignition sources and evacuate area if significant vapor concentration occurs. Ventilate area. Person wearing appropriate protective equipment may then enter the area and contain large spills with dikes, pump to salvage tank if possible and flush the spill area with water or absorb in an inert material.
	DISPOSAL METHOD Dilute with fuel oil and burn this mixture by atomizing it into a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

HEALTH HAZARD DATA	THRESHOLD LIMIT VALUE (PERMISSIBLE EXPOSURE LIMIT) 100 ppm (TLV and PEL)
	EFFECTS OF OVEREXPOSURE Vapors: Headache, nausea, vomiting, narcosis. Chronic overexposure may cause liver and kidney damage. Liquid: Prolonged exposure to skin can lead to mild irritation due to "defatting." Only slightly toxic by ingestion.

FIRST AID	EYE: Nonirritating. If splashed in eye, immediately flush eye with a large quantity of water for at least 15 minutes.
	SKIN: Remove clothing wet with NE; launder before reuse. Wash exposed skin with soap and water.
	INHALATION: Remove to fresh air. Perform artificial respiration if breathing has stopped.
	INGESTION: Induce vomiting by giving victim several glasses of water and placing his finger down his throat.

PROTECTIVE EQUIPMENT	VENTILATION Supply outside air and exhaust fans sufficient to meet the TLV requirement. Use local exhaust for any operation releasing excessive vapors.
	RESPIRATORY PROTECTION Self-contained breathing apparatus should be worn in emergency situations where high vapor concentration occurs.
	PROTECTIVE CLOTHING Rubber gloves for operations which require prolonged exposure.
	EYE PROTECTION Wear safety glasses or chemical goggles; as the situation warrants.

OTHER SPECIAL PRECAUTIONS	PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE Keep away from heat and flame. Keep container closed. Ground all metal containers when transferring liquid. Use only with adequate ventilation.
	SPECIAL COMMENTS Dry NE may be stored in mild steel, but wet NE (>0.2% water by wt) must be stored in stainless steel or aluminum.

Prepared by A. F. Bollmeier, Jr.

Date May 29, 1985

icals. Among these useful derivatives of nitroethane are phenylpropanoamine, amphetamine, amphetaminil, and phenylacetone.

Dimethoxyphenylacetone, a raw material for the manufacture of α -methyl dopa, is readily synthesized by reaction of 3,4-dimethoxybenzaldehyde with nitroethane, followed by catalytic hydrogenation and hydrolysis.

The insecticide methomyl is conveniently prepared by the treatment of the potassium salt of nitroethane with methyl mercaptan and methanol.

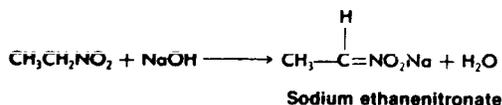
For further, more detailed information on the uses of nitroethane in synthesis, ask any ANGUS Representative for assistance with specific reaction or reaction type of interest.

Chemical Reactions

The chemical reactions presented in this data sheet are representative but not by any means comprehensive. A number of review articles which provide additional detailed information on nitroparaffin chemistry have been written.¹⁻⁴

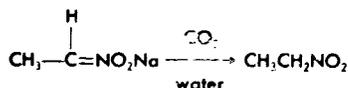
REACTION WITH STRONG BASE

Nitroethane slowly reacts with strong bases such as sodium hydroxide to form nitronate salts.⁷

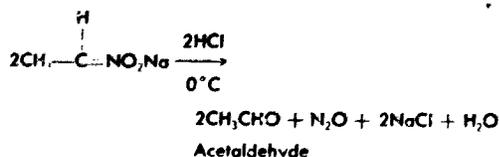


CAUTION: Dry metallic salts of nitroethane may be ignitable; keep them away from sparks and flame.

The acidification of sodium ethanenitronate with weak acids, such as CO_2 , regenerates nitroethane.⁸

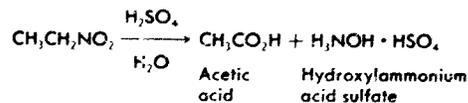


If mineral acids are used under mild conditions, the nitronate salt decomposes into acetaldehyde and nitrous oxide.⁹

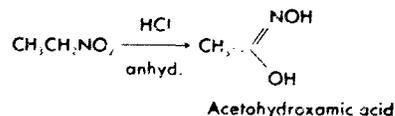


REACTION WITH STRONG ACID

Nitroethane reacts with hot concentrated mineral acids to yield acetic acid and a hydroxylamine salt.¹⁰

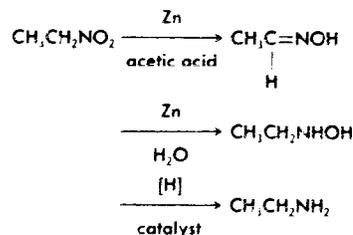


The intermediate hydroxamic acid can be obtained under anhydrous conditions at lower temperature.¹⁰



REDUCTION

Nitroethane may be reduced to yield acetaldoxime, *N*-ethylhydroxylamine, or ethylamine depending on the reaction conditions chosen.¹¹



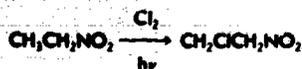
HALOGENATION

Nitroethane is readily chlorinated by treatment with sodium hypochlorite. One or both of the hydrogen atoms on the carbon holding the nitro group can be replaced with halogens.²



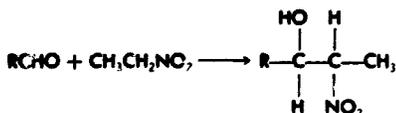
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Under anhydrous conditions β -chloronitroethanes can be formed by exposure of a chlorine-nitroethane mixture to strong irradiation with visible light.¹²

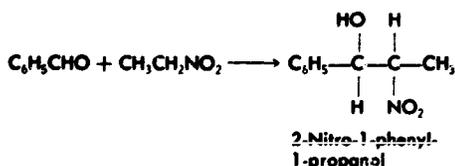
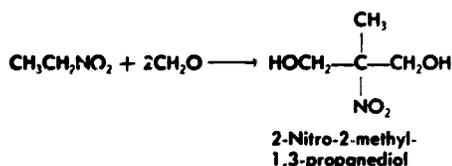


CONDENSATION WITH ALDEHYDES

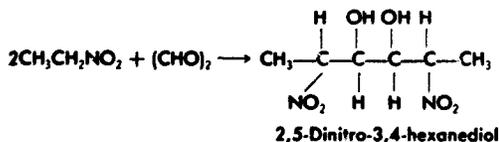
Nitroethane reacts with aldehydes to yield nitro alcohols.²



Both of the hydrogen atoms on the carbon holding the nitro group can be displaced by formaldehyde, but only one mole of higher aliphatic aldehydes or aromatic aldehydes can be added to nitroethane.²



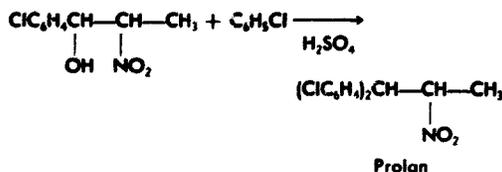
The reaction of a dialdehyde, such as glyoxal, with two moles of nitroethane is a convenient method for preparing dinitro compounds.¹³



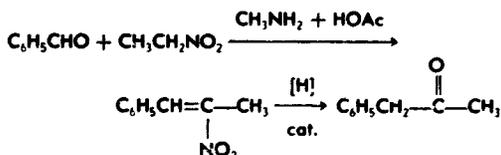
The nitrohydroxy compounds can be reduced readily to their amino analogs or dehydrated to nitro olefins. See ANGUS Series Technical Data Sheets 15 and 10 for further information on the chemical properties of the

nitro alcohols and amino alcohols.

The insecticide Prolan can be synthesized from 2-nitro-1-*p*-chlorophenyl-1-propanol by reaction with chlorobenzene in sulfuric acid.¹⁴

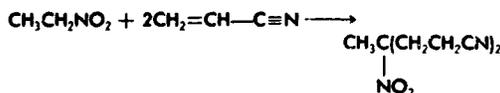
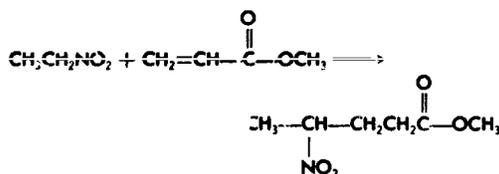


Phenylacetone can be synthesized by a two-step process in which benzaldehyde and nitroethane, in the presence of monomethylamine acetate, react to yield a nitro olefin which is then catalytically reduced.^{15,16}



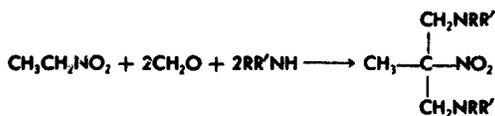
CONDENSATION WITH ACTIVATED OLEFINS

Nitroethane reacts with activated double bonds under the influence of basic catalysts. These Michael condensations can be controlled so that nitroethane adds to either one or two moles of the activated olefin.^{17,18}

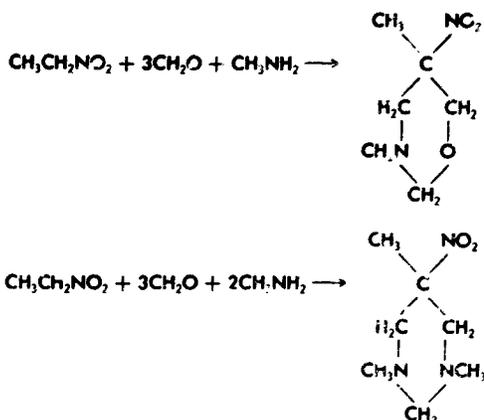


MANNICH-TYPE REACTIONS

Nitroethane reacts with formaldehyde and amines in one step to yield Mannich bases.^{19,20}

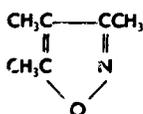


With primary amines and an excess of formaldehyde, this reaction proceeds to nitro-substituted cyclic derivatives.^{19,20}

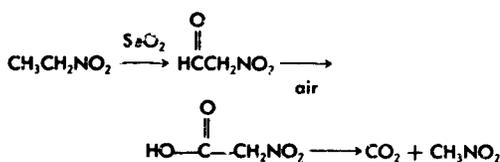


OXIDATION

The oxidation of nitroethane by peroxysulfate yields 3,4,5-trimethylisoxazole.²¹

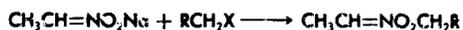


When selenium dioxide is used as the oxidizer, α -nitroacetaldehyde is formed in low yield. However, on exposure to air this compound is readily oxidized to nitroacetic acid, which spontaneously decomposes into CO_2 and nitromethane.²²

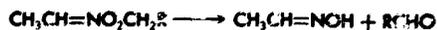


ALKYLATION REACTIONS

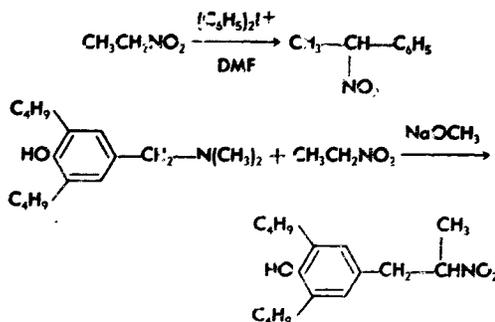
The salts of nitroethane most often do not react with alkyl or aryl halides. In some cases they undergo O-alkylation to produce nitronic esters.



The nitronic esters are usually unstable and decompose rapidly into acetaldoxime and aldehyde.

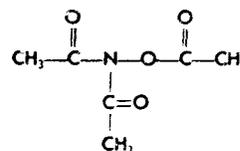


However, C-alkylation has been accomplished in a few specific instances.^{23,24}



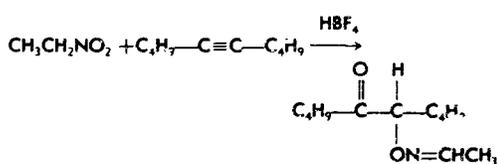
OXIDATIVE ACYLATION

The treatment of nitroethane on a steam bath with acetic anhydride in the presence of sodium acetate produces in high yield a compound with the following structure:²⁵



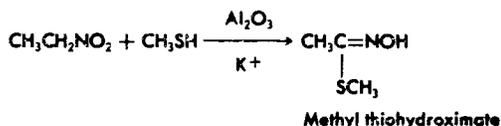
REACTION WITH ALKYNES

Nitroethane, in the presence of HBF_4 , reacts with alkynes to add a proton and the acinitroethane to the triple bond.²⁶



REACTION WITH MERCAPTANS

Thiohydroxamic esters which are useful as insecticides and acaricides can be prepared by the reaction of nitroethane or its salts with mercaptans.²⁷



References

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Typical Properties of Commercial-Grade Nitroethane

Distillation range at 1 atm (90% min.), °C...	112-116
Vapor density (air = 1)	2.58
Specific gravity at 25/25°C	1.045
Change of density with temperature, 0-50°C, g/(ml. °C)	0.0012
Weight per U.S. gallon at 68°F, lb	8.75
Flash point, Tag open cup, °F	106
Tag closed cup, °F	87
Lower limit of flammability, % by vol (at 30°C)	3.4
Ignition temperature, °C	414
Evaporation rate (n-butyl acetate = 100) ..	121
Evaporation number (diethyl ether = 1) ...	11

Physical Properties of Nitroethane

Molecular weight (calcd.)	75.068
Boiling point at 760 mmHg, °C	114.07
Vapor pressure at 25°C, mmHg	20.93
Freezing point, °C	-89.52
Density at 20°C, g/ml	1.051
at 30°C, g/ml	1.039
Coefficient of expansion per °C	0.00112
per °F	0.00062
Refractive index, n_D , at 20°C	1.39193
at 30°C	1.38754
Surface tension at 20°C, dynes/cm	32.66
Viscosity at 20°C, cp	0.677
at 30°C, cp	0.602
Heat of combustion (liq.) at 25°C, kcal/mole	-325.6
Heat of vaporization (liq.) at 25°C, kcal/mole	9.94
at bp, kcal/mole	9.08
Heat of formation (liq.) at 25°C, kcal/mole	-33.9
Specific heat at 25°C, cal/(mole·°C)	33.10
at 25°C, cal/(g·°C)	0.441
Dielectric constant at 30°C	28.06
Dipole moment, μ , gas, Debye units	3.58
liquid, Debye units	3.19
pH of 0.01M aqueous solution	6.0
Solubility in water at 20°C, % by wt.	4.6
at 25°C, % by wt	4.7
at 70°C, % by wt	6.6
Solubility of water in NE at 20°C, % by wt	0.9
at 25°C, % by wt	1.1
at 70°C, % by wt	3.0
Hydrogen bonding parameter, γ	2.5
Solubility parameter, δ	11.1

Toxicity

ORAL

The acute oral LD₅₀ for nitroethane in the Sprague-Dawley strain of rat is estimated to be 1625 ± 193 mg/kg of body weight. Thus, nitroethane is classified by toxicologists as slightly toxic following oral administration since it is within the toxic range of 500 to 5000 mg/kg. Should accidental ingestion occur, promptly induce vomiting.

DERMAL ABSORPTION

In a dermal application to rabbits, a nitroethane dose of ~~200~~^{1,000} mg/kg of body weight was not absorbed in lethal amounts. There were no deaths nor any signs of significant gross toxicity.

EYE AND SKIN IRRITATION

A dose of 0.1 ml of undiluted nitroethane instilled into the eyes of rabbits produced no significant degree of toxicity or irritation. Likewise, the product was nonirritating to the abraded and unabraded skin of rabbits. Prolonged or frequently repeated exposure may cause defatting and drying of the skin in a manner similar to that experienced with most other organic solvents.

If nitroethane is splashed in the eyes, flush eyes well with water. In case of accidental spillage on skin and clothing, wash well with soap and water and change to clean clothing.

VAPOR INHALATION

The American Conference of Governmental Industrial Hygienists has established a threshold limit value for nitroethane of 100 ppm (310 mg/m³) as a time-weighted average concentration for an 8-hour workday and a 40-hour workweek. This value has been adopted as a permissible limit by the Occupational Safety and Health Administration, U.S. Department of Labor (cf. 29 CFR 1910.1000). Excursions to a ceiling limit of 150 ppm for 15-minute periods separated by at least 60 minutes should not be exceeded. If exposure to vapors of nitroethane above the permissible exposure limit is anticipated, a self-contained breathing apparatus should be used. Canister-type

masks are not recommended. Remove an exposed individual to fresh air at once; get medical attention.

Vapor-inhalation studies employing 6-hour daily exposure periods show that a concentration of nitroethane of 550 ppm (1552 mg/m³) is nonlethal to rats following 12 repeated exposures during a 21-day period.

Rats survived five 6-hour inhalation sessions at a vapor concentration of 2200 ppm (6.8 g/m³) with no noticeable difficulty.

Nitroethane is fatal to rats in 6-7 hours during the course of exposure to an atmosphere containing 13,000 ppm.

METABOLIC STUDIES

Nitroethane when administered orally or intravenously to rabbits is partially excreted unchanged by the lungs. The amount of nitroethane found in tissues decreases at a fairly rapid rate. Metabolic products of nitroethane appear to be acetaldehyde and nitrite.

Intraperitoneal injection of nitroethane at a dose of 1.1 g/kg in rats was not fatal, whereas 1.6 g/kg caused death in 10-15 hours. Nitroethane was recovered from the liver and exhaled air; nitrites were found in the heart, lung, kidney, and spleen tissues and in urine. Methemoglobinemia may be a consequence associated with these nitrites.

Precautionary Labeling

Labels for **NE** bear these caution statements:

CAUTION! FLAMMABLE.

Keep away from heat, sparks, and flame.

Use only with adequate ventilation.

Avoid prolonged breathing of vapor.

Keep container closed.

Dry salts formed with strong alkalis may be ignitable; keep them away from heat, sparks, and flame.

In case of fire, use water spray, foam, or CO₂; use only dry chemical, triclass extinguishers approved for class ABC fires.

Flush spill area with water spray.

FOR INDUSTRY USE ONLY

Storage and Handling

Nitroethane should be handled in a manner similar to that of any other volatile organic solvent. Avoid prolonged breathing of nitroethane vapors, and use only with adequate ventilation. Keep containers closed. In case of spills, flush spill area with water spray but not into sewers where vapors may become ignited.

Because it has a flash point of 87°F by Tag closed cup, nitroethane is considered flammable under the definitions of the U.S. Department of Transportation. Keep it away from heat, sparks, and flame. Use nonsparking tools when opening containers.

Water spray, foam, or CO₂ can be used to control and extinguish burning nitroethane. Use dry chemical triclass extinguishers (those containing only ammonium phosphate and rated for ABC fires) on small nitroethane fires. Dry chemical fire extinguishers which contain sodium or potassium bicarbonate are not rated for use with class A fires. Such extinguishers only appear to put out nitroethane fires when first applied but later contribute to reignition.) As in the case with all chemical fires, self-contained breathing apparatus should be worn when fighting large fires.

For detailed information on materials of construction, storage tanks, pumps, piping, valves, hoses, and polymers consult one of the ANGUS Technical Data Sheets on the nitropropane solvents.

Only under conditions of extreme shock and heavy confinement at elevated temperatures is there any tendency for nitroethane to exhibit explosive decomposition. When allowed to react with alkalis, such as sodium hydroxide, nitroethane forms nitronate salts. When dry, such salts may be ignitable from static electricity or other spark sources. The dry salts also can decompose violently if confined and subjected to elevated temperatures (e.g., 180°C for the sodium salt). Thorough testing should be carried out on the specific product before any attempt is made to produce, use, or ship the dry salts on a large scale. Do not use caustic soda or lye to clean equipment containing nitroethane unless it is thoroughly flushed with water as a final step in the cleaning.

When emptied, drums which contained nitroethane should be cleaned for reuse by filling to overflowing with water followed by thoroughly rinsing several times with water. Do not cut, puncture, or weld any drum unless it has been cleaned.

Shipping Containers

Nitroethane is available in tank cars or tank trucks; in DOT 17E 55-gallon drums, 475 lb net weight; in 5-gallon drums, 43 lb net weight; and in 1-gallon cans, 8 lb net weight.

DOT Proper Shipping Name:

Flammable Liquid NOS

DOT Hazard Class:

Flammable Liquid

Identification No.: UN 1933

IMCO Class: 3.3

Azeotropes with Nitroethane

Compound	B.p., °C	Azeotrope	
		Wt % of Compound	B.p., °C
Propyl nitrate	110.5	<79	<109.6
Propyl alcohol	97.2	68.2	94.5
Isopropyl alcohol	82.4	89.4	81.8
1-Bromobutane	101.5	75	96.0
1-Bromo-2-methylpropane	91.4	90	89.5
Butyl alcohol	117.8	45	107.7
sec-Butyl alcohol	99.5	72.4	97.2
t-Butyl alcohol	82.4	95.5	82.2
Isobutyl alcohol	108.0	60	102.5
1-Bromo-3-methylbutane	120.6	<45	<108.5
Amyl alcohol	138.2	<17	<137.8
t-Amyl alcohol	102.4	<70	<98.6
Isoamyl alcohol	151.0	22	112.0
Methylcyclopentane	72.0	<96	<71.2
4-Methyl-2-pentanone	116.0	—	<113
Ethyl butyrate	121.5	<27	<113.7
Ethyl isobutyrate	110.1	73	108.5
Isobutyl acetate	117.4	40	112.5
Isopropyl sulfide	120.5	<40	<110.9
Toluene	110.8	75	106.2
Methylcyclohexane	101.2	70	90.8
n-Heptane	98.4	72	89.2
2,2-Dimethylhexane	109.4	<38	<96.9
Acetic acid	114.2	30	112.4
Water	100.0	28.5	37.2
Ethyl alcohol	78.3	87.4	78.0

Nitroethane is reported not to form azeotropes with benzene or methanol.

The information and data contained herein are believed to be correct. However, we do not warrant either expressly or by implication the accuracy thereof. In presenting uses for this product, no attempt has been made to investigate or discuss any patent situations which may be involved.

HBV