NMPD

2-NITRO-2-METHYL-1,3-PROPANEDIOL

$(CH_2OH)_2C(NO_2)CH_3$ Mol. Wt. 135.12

csc

ACTIVE INGREDIENT **100%**
2-Nitro-2-methyl-1,3-propanediol

CAUTION! Harmful if swallowed

FOR MANUFACTURING USE ONLY

C-76C

USDA Registration No. 271-20

Nitroparaffins Industrial Corporation

ACCEPTED

MAR 19 1969

UNDER THE FEDERAL INSECTICIDE, FUNGICIDE AND RODENTICIDE ACT FOR ECONOMIC POISON REGISTERED UNDER NO. 271-20 SUBJECT TO ATTACHED COMMENTS.

NP TDS No. 15
draft of:
January 13, 1969

ESC® NITROHYDROXY COMPOUNDS

NB	2-Nitro-1-butanol	$CH_3CH_2CH(NO_2)CH_2OH$
NMP	2-Nitro-2-methyl-1-propanol	$CH_3C(CH_3)(NO_2)CH_2OH$
NMPD	2-Nitro-2-methyl-1,3-propanediol	$HOCH_2C(CH_3)(NO_2)CH_2OH$
NEPD	2-Nitro-2-ethyl-1,3-propanediol	$HOCH_2C(C_2H_5)(NO_2)CH_2OH$

GENERAL

These nitrohydroxy compounds are produced for the chemical industry as raw materials for synthesis. They enter into a variety of chemical reactions and, since the nitro group can be reduced readily to the amine, they offer possibilities for synthesis of dyes, pharmaceuticals, and surface active agents. They also possess varying degrees of effectiveness as biocides, but to a somewhat lesser extent than does tris(hydroxymethyl)nitromethane. Tris Nitro® brand of tris(hydroxymethyl)-nitromethane is described in detail in NP Technical Data Sheet No. 5.

Except for 2-nitro-1-butanol, all of these nitrohydroxy compounds are colorless, crystalline solids. Although quite stable at ordinary temperatures, they will decompose when heated. When exposed to alkaline materials, the nitrohydroxy compounds yield formaldehyde. The rate of release can be controlled by pH and temperature; thus the nitrohydroxy compounds may be used as formaldehyde donors in specialty products such as adhesives or foundry resins where efficient utilization of the formaldehyde and minimum odor are essential.

2-Nitro-1-butanol is a liquid of low vapor pressure which possesses strong solvent power for many polyamide resins, as well as zein,

nitrocellulose, cellulose acetate butyrate, and ethylcellulose. It is used as a "fugitive" plasticizer and evaporation retarder in printing inks to control flow.

The nitrohydroxy compounds are soluble in water or alcohols, but are insoluble in aliphatic hydrocarbons. The monohydric alcohols are soluble in aromatic hydrocarbons; the diols are only moderately soluble even at 50°C.

CSC Specifications	NB	NMF	NMPD	NEPD
Melting point (min.)	-	80°C	150°C	40°C
Water (max.)	6.0% by wt	0.5% by wt	0.5% by wt	0.5% by wt
Free formaldehyde (max.)	0.2% by wt	0.04% by wt	0.04% by wt	0.04% by wt
pH of 20% aqueous solution	-	4.0-6.5	3.5-7.0	4.0-6.5
Color of 20% aqueous solution (max.)	1 Gardner	40 APHA	1 Gardner	40 APHA

Physical Properties of Purified Materials	NB	NMP	NMPD	NEPD
Molecular weight (calc.)	119.12	119.12	135.12	149.15
Melting point	-47 to -48°C	90°C	ca. 160°C	56°C
Boiling point at 10 torr	105°C	-	decomposes	decomposes
at 15 torr	-	94°C	-	-
pH of 0.1M solution at 20°C	4.5	5.1	5.4	5.5
Density at 25°C	1.129 g/ml	-	-	-
Weight per U.S. gallon at 68°F	9.43 lb	-	-	-
Coefficient of expansion per °C	0.00076	-	-	-
Refractive index, n_D at 20°C	1.444	-	-	-
Evaporation rate (n-butyl acetate = 100)	<1	-	-	-
Flash point	227°F	-	-	-
Surface tension at 20°C	37.7 dynes/cm	-	-	-
Solubility in 100 ml water at 20°C	54 g	350 g	80 g	400 g
Solubility of water in 100 ml NB	88 g	-	-	-

ANTIMICROBIAL USES

Certain nitrohydroxy compounds are useful preservatives for aqueous systems, especially at a slightly alkaline pH. Such systems as cutting oils and emulsions can be kept substantially free from microbial growth by a concentration of 0.1-0.5%, depending on the composition of the system and the degree of contamination (5). While this range of concentration probably will be satisfactory for most systems, users should test these materials under their particular conditions to determine the best method of using the product.

The following antimicrobial spectrum indicates the effectiveness of 2-nitro-2-methyl-1,3-propanediol and 2-nitro-2-ethyl-1,3-propanediol.

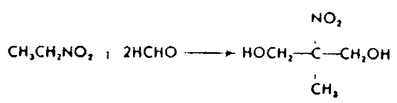
	Inhibitory Concentration, µg/ml	
Organism	NMPD	NEPD
Staphylococcus aureus	500-1000	500-1000
Streptococcus fecalis	1000	500-1000
Streptococcus hemolyticus	500-1000	500-1000
Escherichia coli	>1000	>1000
Pasteurella pseudotuberculosis	500-1000	100-500
Shigella dysenteriae	500-1000	100-500
Mycobacterium 607	500-1000	500-1000
Mycobacterium ranae	>1000	>1000

Using the method of Wheeler and Bennett (25) for measuring the effectiveness of antimicrobial agents in cutting oils, the following results were obtained.

Concentration of Nitrohydroxy Compound	Duration of Effectiveness	
	NMPD	NEPD
1,000 ppm	105 days	134 days
500	98	111
100	72	7

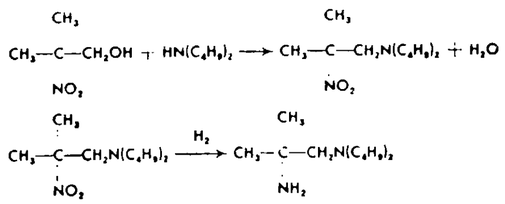
CHEMICAL REACTIONS

These nitrohydroxy compounds are made by condensing a nitroparaffin with formaldehyde; e.g.:



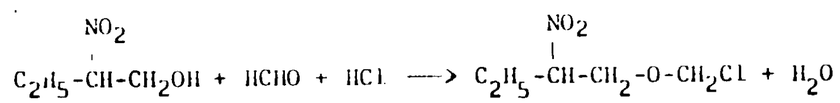
In the presence of an alkaline substance, this reaction is reversible to yield free formaldehyde and the original nitroparaffin. The reversal is quantitative and is the basis of an analytical procedure for nitrohydroxy compounds in which the released formaldehyde is measured. (Tris Nitro is an exception for it releases only two moles of formaldehyde instead of the expected three.)

Nitro alcohols react with primary or secondary amines to form the nitro amine, which in turn can be reduced (10) to form the N-substituted diamine:



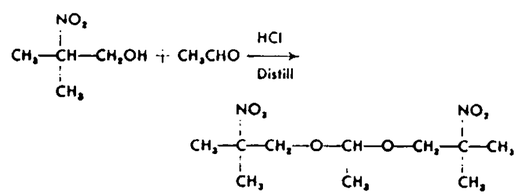
If the nitrohydroxy compound is a diol, then the nitro diamine is formed (17); and if a nitro diol and a polyamine are employed, a polymer is obtained (1).

2-Nitro-1-butanol and 2-nitro-2-methyl-1-propanol react with formaldelyde and hydrogen chloride to form the chloromethyl ether (3,9); e.g.:



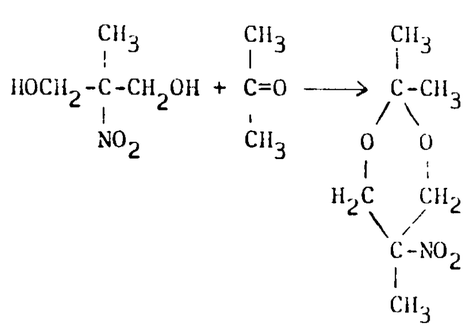
The chlorine in such a compound is very reactive, so this product can be employed in further reactions.

If higher aldehydes condense with nitro alcohols, nitro acetals are obtained (18, 19, 21):



These nitro acetals can be reduced to amino acetals (22).

Nitro diols react with aldehydes and ketones to form substituted acetals or ketals known as nitro dioxanes (14, 20):

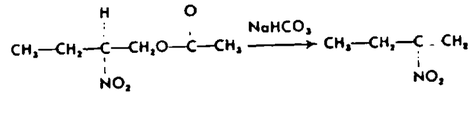


Esters of nitrohydroxy compounds are prepared readily from organic and inorganic acids or anhydrides in the presence of the usual esterification catalysts (6, 7, 15). Tindall (23) has reported the preparation of 96 nitro esters. Some of these esters have potentially interesting properties. For example, fatty acid esters can be applied to textiles for waterproofing (16, 24), and the maleic and fumaric esters of 2-nitro-1-butanol or 2-nitro-2-methyl-1-propanol produce unique copolymers with butadiene (13). Nitro esters also may have

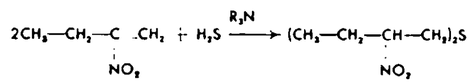
utility as stabilizers for petroleum lubricants (4).

The nitrate esters form easily on treating the nitro alcohols with the same nitric acid--sulfuric acid mixture that is used for the manufacture of nitroglycerin. The resulting products have good explosive properties, and apparently only their cost has prevented their industrial utilization.

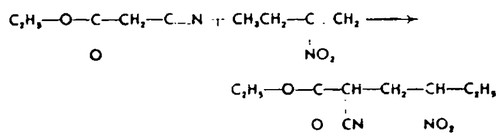
The acetate esters of primary and secondary nitro alcohols such as 2-nitro-1-butanol are useful intermediates for the preparation of nitro olefins:



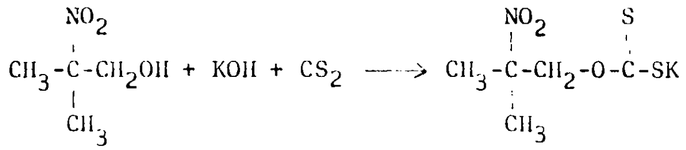
Nitro olefins can be used as intermediates in numerous reactions, most of which are typical of olefins. For instance, hydrogen sulfide will add directly to 2-nitro-1-butene (2):



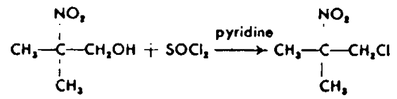
and nitro olefins condense with cyanoacetic esters to form nitrocyano esters (3):



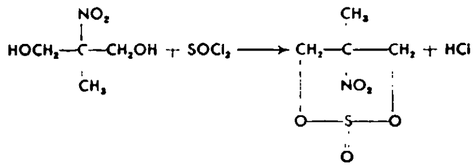
If nitrohydroxy compounds react with carbon disulfide, nitro-substituted xanthates are formed:



Thionyl chloride will convert monohydroxy nitro compounds to chloronitroparaffins (11):



With nitro diols or Tris Nitro, the nitroalkyl sulfite is formed (12):



TOXICITY

Because these nitrohydroxy compounds have low volatility, there is no hazard from vapor inhalation. They are only slightly toxic by oral administration, as shown by the following data.

Acute Oral Toxicity in Mice

Product	LD_{50}, g/kg
2-Nitro-1-butanol	1.2
2-Nitro-2-methyl-1-propanol	1.0
2-Nitro-2-methyl-1,3-propanediol	4.0
2-Nitro-2-ethyl-1,3-propanediol	2.8

These nitrohydroxy compounds are nonirritating to human skin and, with the exception of 2-nitro-1-butanol, are nonirritating when introduced as a 1% aqueous solution into the eye of a rabbit. Commercial-grade 2-nitro-1-butanol produces severe irritation and permanent corneal scarring when tested by introducing 0.1 ml undiluted into the eyes of rabbits. It is possible that a small amount of 2-nitro-1-butene is present in the commercial-grade material; nitro olefins are known to be extremely irritating to the eyes and mucous membranes. The other nitrohydroxy compounds are recrystallized products, so nitro olefins are not present.

SHIPPING, STORAGE, AND HANDLING

The nitrohydroxy compounds should be protected from moisture, alkaline vapors such as ammonia or amines, and excessive heat. Crystalline nitrohydroxy compounds are shipped in fiber containers. The crystalline nitrohydroxy compounds are more stable with respect to thermal decomposition than is 2-nitro-1-butanol but, nevertheless, they should be stored in a cool, dry place. All these compounds show an increasing rate of decomposition as the temperature is raised. 2-Nitro-2-methyl-1-propanol begins to decompose at about 120°C; the others show varying rates of decomposition at temperatures above 100°C.

2-Nitro-1-butanol is shipped in coated steel drums. This liquid product can be conveniently stored and handled in type 2S aluminum, type 304 stainless steel, or glass, but it does not show satisfactory storageability in ordinary steel. 2-Nitro-1-butanol should be stored at temperatures of 35°C or less, since at higher temperatures some pressure build-up occurs over a period of weeks due to the evolution of noncondensable gas. Do not attempt to distill

2-nitro-1-butanol at temperatures above 100°C, since rapid decomposition is apt to occur with the evolution of large quantities of gas. Distillation pressures of 5-10 torr have been used without difficulty.

SHIPPING CONTAINERS

	Net Weight, lb		
	55-gal drum	5-gal drum	1-gal can
2-Nitro-1-butanol	500	45	9
	51-gal Lever-pak*	5-gal Fiber-pak	1-gal Fiber-pak
2-Nitro-2-methyl-1-propanol	225	25	5
2-Nitro-2-methyl-1,3-propanediol	250	25	5
2-Nitro-2-ethyl-1,3-propanediol	250	25	5

*Polyethylene-Lined