RE: WCBCJ0411

NON-CONFIDENTIAL BUSINESS INFORMATION

LISTING BACKGROUND DOCUMENT 1,1-DIMETHYLHYDRAZINE (UDMH) PRODUCTION FROM CARBOXYLIC ACID HYDRAZIDES

- K107 Column bottoms from product separation in the manufacture of UDMH (1,1-dimethylhydrazine) using carboxylic acid hydrazides (C,T)
- K108 Condensed column overheads from product separation and condensed reactor vent gases in the manufacture of UDMH (1,1-dimethylhydrazine) using carboxylic acid hydrazides (T)
- Kl09 Spent filter cartridges from product purification in the manufacture of UDMH (1,1-dimethylhydrazine) using carboxylic acid hydrazides (T)
- K110 Condensed column overheads from intermediate separtion in the manufacture of UDMH (1,1-dimethylhydrazine) using carboxylic acid hydrazides (I,T)

TABLE OF CONTENTS



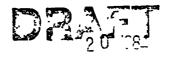
I.	SUMM	ARY OF BASIS FOR LISTING
II.	SOUR	CES OF WASTE AND TYPICAL DISPOSAL PRACTICES4
	Α.	Industry Profile4
	В.	Manufacturing Process4
	С.	Waste Generation and Management
	D.	Waste Composition8
III.	BAS	IS FOR LISTING10
		• -
	Α.	Hazards Posed by the Listed Wastes and Wastes Contituents
	В.	Potential for Mismangement10
	с.	Environmental Fate and Transport; Migration, Mobility, and Persistencell
	D.	Health Effects
	E.	Existing Regulations and Guidelines15
IV.	REI	FERENCES



I. SUMMARY OF BASIS FOR LISTING

The unique proprietary manufacturing process to produce 1,1-dimethylhydrazine (UDMH) by Uniroyal, Inc. generates four liquid wastes containing hazardous concentrations of UDMH and in some cases methanol, ethanol, and sodium hydroxide. These wastes are all toxic, and in some cases ignitable or corrosive. The Administrator has determined that these wastes are solid wastes that may pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, disposed of, or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- These wastes contain significant concentrations of 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH), which has been determined by the U.S. EPA's Carcinogen Assessment Group (CAG) to be a potential human carcinogen.
- 2. The condensed column overheads from product separation and condensed reactor vent gases also contain significant concentrations of alcohols, making this waste ignitable. The column bottoms from product separation contain significant concentrations of sodium hydroxide, making this waste corrosive.
- 3. A significant volume of these wastes (5000 metric tons or 11 million pounds) are generated annually, increasing the opportunity for hazardous exposures if mismanagement occurs.
- 4. UDMH is mobile and persistent in ground water under conditions approximating waste disposal. Therefore, ground water contamination is possible under conditions approximating waste disposal if deep well injection techniques (the current disposal practice for the purification column light ends and bottoms) are improperly conducted or if the wastes are mismanaged during storage or disposal in unlined or inadequately lined land disposal facilities.



II. SOURCES OF WASTE AND TYPICAL DISPOSAL PRACTICES

A. Industry Profile

1,1-Dimethylhydrazine, commonly known as unsymmetrical dimethylhydrazine (UDMH), is manufactured via a unique proprietary process by Uniroyal, Inc. This UDMH product is presently not marketed commercially but is produced solely as an intermediate for Uniroyal products. Current production figures are unavailable.

The Olin Corporation also manufactures UDMH by a different chemical process than that employed by Uniroyal. This process will be evaluated separately because the process chemistry involved is expected to yield wastes with different characteristics.

Olin's product is sold commercially, and finds use as a rocket fuel, and to a smaller extent, as an absorbent for acid gases, in the manufacture of various photographic chemicals, and as a stabilizer for organic peroxide fuel additives. Another use for Olin's product is as an analytical reagent for aldehyde and ketone analysis.

B. Manufacturing Process

A complete description of the Uniroyal manufacturing process and process chemistry, provided by the manufacturer in response to a questionnaire under Section 3007 of the Resource Conservation and Recovery Act (RCRA), has been claimed to be confidential business information by Uniroyal, and therefore is not presented here. Readily available information in the technical literature (Kirk-Othmer), however, states that UDMH is probably made (by Uniroyal) by the reductive catalytic alkylation of a carboxylic acid hydrazide with formaldehyde and hydrogen, followed by basic hydrolysis of carboxylic acid dimethylhydrazide to



remove the carboxyl group, as shown in the following equation.

$$\begin{array}{ccc} & \text{CH}_2\text{O}/\text{H}_2\text{O} & \text{base} \\ \text{RCONHNH}_2 & ----- & \text{RCONHN}(\text{CH}_3)_2 & ----- & (\text{CH}_3)_2\text{NNH}_2 \end{array}$$

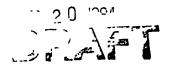
Figure 1 shows this conversion with the associated waste and process streams. Triangles indicate streams in the gaseous state, while circles indicate streams in the liquid state and squares represent wastes in the solid state. This figure has been generalized so as to protect confidential process information.

C. Waste Generation and Management

There are three liquid waste streams and one solid waste stream generated by this process, described below and keyed to Figure 1.

The primary waste that is generated is the column bottoms from the final purification step to produce commercial UDMH (Liquid Stream 4, Waste No. K107). This waste is currently managed by injection in a 3000 ft. deep well on the plant premise after holding in a concrete-lined surface impoundment. Approximately 2,810 metric tons of this waste are generated annually. Sludges are accumulated in the concrete-lined surface impoundment* from holding the product purification bottoms along with other wastes from Uniroyal's facility.

^{*} Uniroyal has indicated they will incinerate these sludges pending completion of an on-site incinerator.



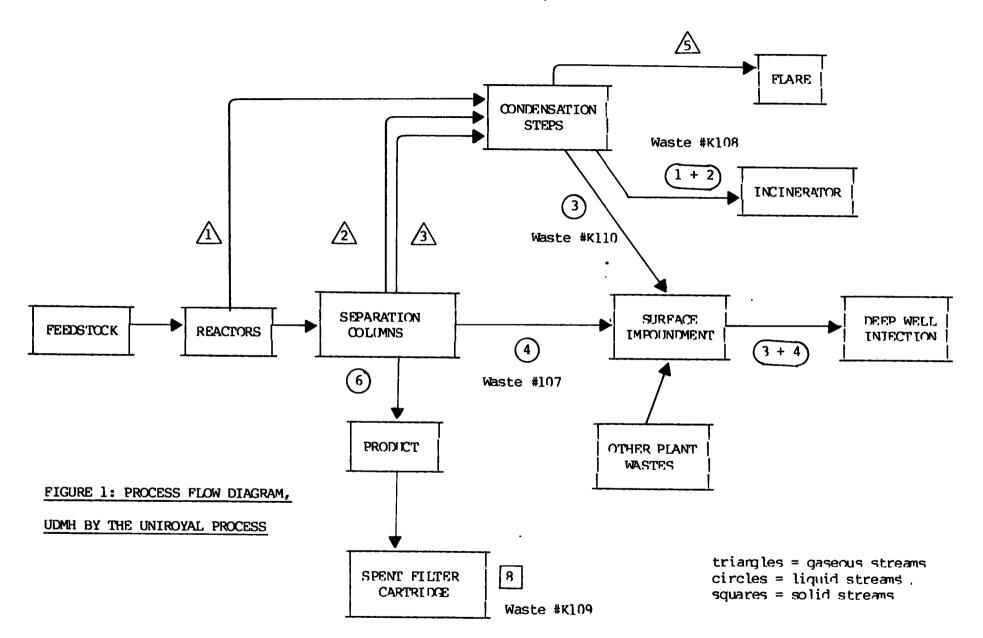
The second listed waste is the condensed overheads from a combination of reactor vent gases (Gas Stream 1) and product separation vent gases (Gas Stream 2), which are co-condensed to generate a liquid waste (Liquid Stream 1+2, Waste No. K108). This waste is incinerated off-site or injected in a deep well off-site. Approximately 91 metric tons of this waste are generated anually.

The third listed waste is spent filter cartridges from product purification (Solid Stream 8, Waste No. K109).

This residual has not yet required removal and disposal. At the time when disposal is required, the company plans to use a permitted hazardous waste diposal facility. The quantity of this waste is judged to be small, since only a small fraction of the facility's UDMH is passed through filter cartridges.

The fourth listed waste is condensed overheads from intermediate separation columns (Liquid Stream 3, Waste No. Kl10) which is codisposed with the product separation column bottoms (Stream 4, Waste No. Kl07) in the surface impoundment, prior to deep well injection on-site.

The uncondensed fractions of Gas Streams 1, 2 and 3 are flared at Gas Stream 5.



D. Waste Composition



Table 1 shows the approximate concentrations of the toxicant of concern in the wastes generated by Uniroyal's proprietary UDMH process, along with the volume generated.

The bottoms from the product separation column (Waste No. K107) contain approximately 0.01 per cent (100 ppm) of UDMH, according to information supplied by Uniroyal. This waste is also corrosive, due to high sodium hydroxide content.

The condensed overheads from product separation and condensed reactor vent gases (Waste No. K108) contain 1-10 per cent (10,000 to 100,000 ppm) of UDMH, according to company supplied information.

The spent filter cartridges from products purification (Waste No. K109) are estimated by the Agency to contain 40-50 per cent (400,000 to 500,000 ppm) of UDMH. This is based on the concentrations of similar liquids entrained in filter cartridges through which they are passes.

The condensed intermediate separation column overheads

(Waste No. K110) have the possibilty of being contaminated with

traces of UDMH at some time, according to Uniroyal, and are therefore

handled as hazardous by Uniroyal because of this possibility.

This waste also contains sufficient concentrations of alcohols to

create an ignitable mixture.

Bottom sediment sludges from the concrete-lined surface impoundment are derived from two listed wastes, Waste No. K107 and K110, and, therefore are also defined as a hazardous waste by 40 CFR § 261.3(c)(2). These sludges could contain significant concentrations of UDMH, as well as toxic waste



Table 1. SUMMARY OF UDMH CONCENTRATIONS IN WASTES & WASTE VOLUME DATA FROM THE PRODUCTION OF UDMH FROM CARBOXYLIC ACID HYDRAZIDES (Reference: Industry Studies 3007 Data Base questionnaire)

Waste No.	Description	Concentrations*	Total Estimated (metric tons)
K107	Column bottoms from product separation	approximately 0.01%	2,810
K108	Condensed column overheads from product separation and condensed reactor vent gases.	1-10%	91
K109	Spent filter cartridges from product purification	40-50%	not yet generated
K110	Condensed column overheads from intermediate separation	trace to 0.01%	1,250

^{*} Hazardous constituent for which the wastes are listed. There is insufficient data to make an accurate determination of the presence of other compounds which should be considered hazardous constituents. If such data becomes available in the future, at that point the may be listed as additional hazardous constituents.



constituents from other processes on the Uniroyal facility.

III. BASIS FOR LISTING

A. Hazards Posed by the Listed Wastes and Wastes Contituents

UDMH is capable of migrating from listed wastes, is mobile

and persistant in the environment, and in situations similar

to waste mismanagement it may reach environmental receptors,

posing a risk to human health and the environment. The following

summarizes experimental information on the environmental fate

and transport and health effects of UDMH. More detailed

information is available in the Health and Environmental

Effects Profile (HEEP) for UDMH.

UDMH is present in these wastes in significant concentrations, typically in concentrations many orders or magnitude above the levels related to the adverse health effects described in the following section. For example, if the condensed column overheads from product separation (the least contaminated waste) were contaminated with even one part per million UDMH, then the concentration would approach one million times the levels related to human health risks in drinking water. The concentration of UDMH in drinking water ingested over a lifetime resulting in a one per million increased risk of cancer is 4.03 x 10⁻⁶ milligrams per liter (parts per million), or 4.03 x 10⁻¹⁰ percent.

B. Potential for Mismangement

The high mobility and migratory potential of the wastes (UDMH and the solvent alcohols in these wastes are



miscible with water) increases the likelihood of harmful exposures under conditions typical of waste management scenarios. Only a fraction of the toxicants present in these wastes need migrate and reach environmental receptors to pose the potential for substantial harm if these wastes are managed improperly.

For example, storage or treatment of these wastes in an unlined surface impoundment could lead to sterilization of the microbial population and the formation of anaerobic conditions beneath the surface impoundment. This could prevent degradation or oxidation of UDMH and allow sufficient quantities to migrate and contaminate ground water. Improper deep well injection could similarly contaminate ground water.

Other examples of potential waste mismanagement practices leading to hazardous exposures could be inadequate incineration or disposal or storage in impoundments or tanks with large open surface areas such that significant volatilization of UDMH occurs.

C. Environmental Fate and Transport; Migration, Mobility, and Persistence.

UDMH is soluble in water in all proportions (miscible) (U.S. EPA, 1980-1984) and is present in wastes which are liquids. The UDMH in these wastes thus has a high mobility and migratory potential. In addition, under conditions typical of waste mismanagement, UDMH is persistent enough to cause harmful exposures. Only a fraction of the toxicant present in these wastes need migrate and reach environmental receptors to pose the potential for substantial harm.

UDMH's low octanol-water partition coefficient and complete miscibility with water indicate that UDMH in any waste contacting soil may migrate and contaminate ground water without being adsorbed onto the soil matrix. UDMH has been shown to leach and migrate in experimental soil columns (Braun, 1983).

The primary degradation mechanism of UDMH in the unsaturated soil zone or aerated surface waters is expected to be oxidation, presumably with dissolved oxygen and free radicals. In the absence of microbial degradation, the half-life of UDMH was reported to be 10 to 14 days in ponds and seawaters (Zirrolli, 1983). In anaerobic conditions, such as in ground water, however, UDMH has the potential for persisting for much longer periods. UDMH was found to be extremely stable in distilled water (Braun, 1983).

The potential for aerobic biodegradation of UDMH in water has not been explored thoroughly, but may be minor relative to oxidation under neutral to basic conditions. UDMH oxidation was found to proceed at the same rate in sterile or non-sterile lake water as well as in pure distilled water (Banerjee; 1977, 1981). Under anaerobic conditions, the loss of UDMH with anaerobic bacteria was 26% after a six-day bioassay. Biodegradation of UDMH may also be limited by its toxicity; aerobic bacterial degradation was inhibited when UDMH concentrations were as low as 20 parts per million (Kane, 1983).

UDMH could also be released to the atmosphere by evaporation from spills, leaks and venting during loading, transfer, storage, or treatment. Evaporation of UDMH from water solutions are expected to be significant (MacNaughton, 1975; Stauffer, 1977). Once volatilized,



UDMH may degrade by reaction with hydroxyl radicals (Pitts, 1981), NO2 or ozone (Tuazon, 1982).

1,1-Dimethylnitrosamine is a potential degradation product of UDMH in the environment, and has also been determined by the U.S. CAG to be a potential human carcinogen.* A major product of the reaction of UDMH with ozone (Tuazon, 1982); however, 1,1-dimethylnitrosamine appears to degrade rapidly in the atmosphere by sunlight (Hanst, 1977; Callahan, 1979; Tuazon, 1982). The formation of 1,1-dimethylnitrosamine may also result from the oxidation of concentrated aqueous solutions of UDMH (Banerjee, 1981), such as would result from spills. The subsequent environmental degradation of 1,1-dimethylnitrosamine is expected to be significantly longer than that of UDMH in water and soil (Tate, 1975; Callahan, 1979; Oliver, 1979; Mallik, 1981).

D. Health Effects

The primary concern of the Agency for the hazardous nature of these wastes is their contamination by significant concentrations of 1,1-dimethylhydrazine (UDMH), which is currently listed in Appendix VIII of Part 261. The U.S. EPA's Carcinogen Assessment Group (CAG) has determined that UDMH is a potential human carcinogen. In addition, N-nitrosodimethylamine (dimethylnitrosamine) is a potential degradation product of volatilized UDMH,* and also has been determined by CAG as a potential human carcinogen.

The major contaminant of concern in these wastes, UDMH,

^{*} The Agency is not listing l,l-dimethylnitrosamine as a toxicant of concern because of uncertainty of the potential degradation pathways of UDMH in the environment. However, the Agency solicits comments as to whether or not l,l-dimethylnitrosamine should be included as a toxicant of concern.



is currently listed in Appendix VIII of Part 261.

When UDMH was administered orally, it produced angiosarcomas, pulmonary adenomas or adenocarcinomas, malignant lymphomas, and kidney adenomas in male and female Swiss mice (Toth, 1972, 1973); tumors in the cecum and blood in Syrian golden hamsters (Toth, 1977); lung tumors in female Swiss mice (Roe et al., 1967); and liver tumors in rats (Druckrey et al., 1967).

Were observed in South African clawed toad larvae, <u>Xenopus laevis</u>, following continuous embronic exposure to UDMH concentrations of 2-20 ug/l (Greenhouse, 1976). UDMH was teratogenic during the neurulation period of embryogenesis, and the malformations affected the head, trunk and tail; the most frequent malformation was tail kinks.

The overall weight of evidence from a variety of microbial and mammalian assays indicates that UDMH is also mutugenic. In numerous Ames Salmonella assays, results were generally inconsistent, although most positive reponses were observed with strain TA98, a frameshift mutant (Bruce, 1979; Parodi et al., 1981; de Flora, 1981). In mutagenesis assays with cultured mouse lymphoma cells, UDMH caused forward mutation to thymidine (Brusick, 1976; Rogers, 1981), but not to ouabain, thioguanine or cytosine arabinoside resistance (Rogers, 1981). Unscheduled DNA synthesis occurred in human embryonic lung cells that were treated with UDMH in vitro (Brusick, 1976), and in vivo exposure to UDMH inhibited testicular DNA synthesis in mice (Seiler, 1977). In vivo treatment of mice also caused DNA fragmentation in liver and lung cells (Parodi, 1981), but did not induce micronuclei in bone marrow cells (Bruce,



1979) or sperm abnormalities (Bruce, 1979; Wyrobek, 1975).

UDMH is rapidly absorbed from the lungs, gastrointestinal tract, injection sites, and skin. Rats exposed to UDMH had grand mal seizures, brain glycogen degradation, and inhibition of glutamic acid decarboxylase (U.S.EPA, 1984).

The Agency has made a preliminary estimate that persons face a 1 per million increased risk of cancer as a result of a lifetime daily dose of 1.15 x 10^{-7} milligrams UDMH per kilogram body weight, or 8.05×10^{-6} milligrams for a 70 kilogram man. The basis for this estimate is explained further in the HEEP. The corresponding concentration in drinking water ingested over a lifetime resulting in a one per million increased risk of cancer is 4.03×10^{-6} milligrams per liter (parts per million), or 4.03×10^{-10} percent.

The potential of this contaminant to cause harm to human health and the environment is described in more detail in the Health and Environmental Effects Profile for UDMH (available at the RCRA Public Docket at EPA Headquarters and at EPA Regional Libraries).

E. Existing Regulations and Guidelines

The Resource Conservation and Recovery Act currently controls the handling (treatmentt, storage, disposal) of the commercial chemical product, 1,1-dimethylhydrazine (UDMH) under 40 CFR §261.33(f); and it is also listed as a hazardous constituent under Appendix VIII of 40 CFR Part 261.

The Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or "Superfund"), requires



that persons in charge of vessels or facilities from which hazardous substances have been released in quantities that are equal to or greater than the reportable quantities (RQs) immediately notify the National Response Center of the release. (See CERCLA Section 103 and 48 FR 23552, May 25, 1983.) Since the statutory RQ for UDMH is one pound, the four waste streams (K107, K108, K109 and K110) will also have RQs of one pound. (Criteria are currently being developed for potential carcinogens such as UDMH to adjust the one pound RQ to a level adequately protective of human health and the environment.)

The Agency's Office of Pesticide Programs (OPP) is also conducting a Special Review (RPAR) process to fully evaluate any dietary risk to human health posed by pesticides containing UDMH or having the possibility of conversion to UDMH. The process was initiated by the finding that UDMH was found to be oncogenic in laboratory animals and that UDMH has been found in raw agricultural commodities (i.e., apples and peaches) and processed foods (i.e., apple sauce and apple juice). In Position Document 1 49 CFR 29136, July 18, 1984, the Agency solicited comments on the risks and benefits associated with all uses of these pesticides, and announced that potential adverse effects associated with the use of these pesticides have been identified and will be examined further to determine their extent and whether, in light of the benefits of the pesticides, such risks are unreasonable. (See 49 CFR 29136, July 18, 1984.)



In addition, The Occupational Safety and Health

Administration (OSHA) has set a Permissible Exposure Limit (PEL)

time-weighted average concentration for UDMH at 1 milligram per

cubic meter of air (0.5 parts per million). The National Institute

for Occupational Safety and Health (NIOSH) has recommended that

this limit be lowered to 0.15 milligrams per cubic meter.

West Germany recommends an occupational exposure limit of 0.1

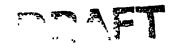
parts per million.

The Department of Transportation (DOT) regulates UDMH as a hazardous flammable material.

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