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Materials Balance 2 - Nitropropane

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Level I — Preliminary



FINAL REPORT

LEVEL I MATERIALS BALANCE

2-NITROPROPANE

Prepared for:

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DISCLAIMER

This is a report on a Level I Materials Balance on 2-nitropropane. As such it is presented as a focus of discussion and as a basis for future materials balance studies: it is not meant to be a definitive study. The results reported were based on a 1,000-hour 10-week analysis of information gathered by JRB staff.

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EXECUTIVE SUMMARY

2-Nitropropane is a clear, colorless liquid that is slightly soluble in water. It is manufactured via the direct nitration of propane by the International Mineral and Chemical Group (IMC) at Sterlington, LA. 2-Nitropropane exists in tautomeric equilibrium with its "aci" or nitronic acid forms as shown below.

The physical properties of 2-nitropropane are represented in the Appendix.

It is estimated that the total consumption of 2-nitropropane in 1979 was approximately 14,000 kkg. Of this amount, about 50 percent was consumed captively to produce 2-nitro-2-methyl-1-propanol, 2-amino-2-methyl-1-propanol, and other aminohydroxy compounds. The remainder was used nonconsumptively, mainly as a solvent. Imports of 2-nitropropane are believed to be negligible (<0.5 kkg per year). Exports of 2-nitropropane amounted to 1,400 kkg in 1979.

An estimated 19 percent (2,700 kkg) of 2-nitropropane is used as a feedstock for the production of 2-nitro-2-methyl-1-propanol, while 31 percent (4,300 kkg) is used as a feedstock in the production of amino-hydroxy compounds. Approximately 21 percent (2,900 kkg) of 2-nitropropane is used as a solvent in printing inks; 12 percent (1,600 kkg) is used as a solvent in surface coating production; and 7 percent (1,100 kkg) of 2-nitropropane is used in miscellaneous uses, including: explosives and propellants, adhesives, dyes, smoke reducers, rubber, and as a solvent and/or extraction agent in various chemical reactions.

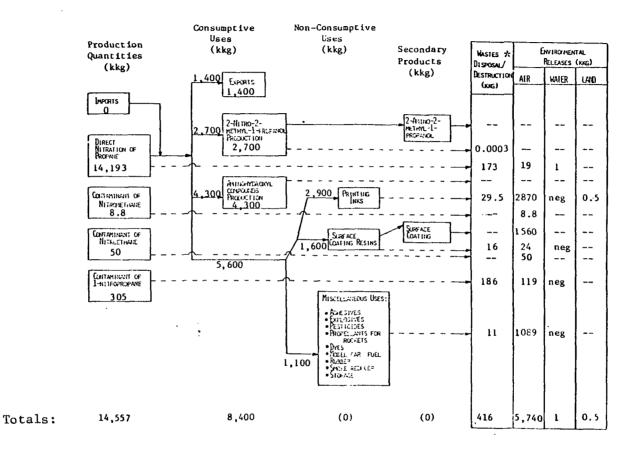
The materials balance for 2-nitropropane is shown in Figure 1. This diagram illustrates the flow of 2-nitropropane in the environment and sources of its release to various media.

Of the estimated 14,000 kkg of 2-nitropropane produced in the United States in 1979, a total of 5,715 kkg (41 percent) is estimated to have been released to the environment. Of these releases, 99.99 percent (5,714 kkg) went to the atmosphere; a negligible amount (1 kkg) went to water. There were no releases to land. An additional 1.6 percent (230 kkg) was destroyed by incineration and waste treatment. These estimates are based on available information and should be verified in later studies.

Most of the releases of 2-nitropropane to air (78 percent or 4,450 kkg) occurred during its use as a solvent in printing inks and surface coatings. The direct production of 2-nitropropane accounts for

only 0.3 percent (21 kkg) of the total releases. No information was available on releases from consumptive uses.

Several major data gaps were encountered during the preparation of this report. Data were lacking on releases from production processes and consumptive and nonconsumptive uses. Another major area where data were lacking was the quantity of 2-nitropropane contaminant in products derived from 2-nitropropane. Finally, there was insufficient information on various minor uses of 2-nitropropane. Resolution of these data gaps would provide a better basis on which to estimate releases of 2-nitropropane.



^{*} These quantities include the amount of 2-nitropropane degraded during waste water treatment and destroyed during incineration

Figure 1 Flow Diagram of the Materials Balance of 2-Nitropropane (1979)

1.0 INTRODUCTION

This report presents the results of a Level I Materials Balance for 2-nitropropane. This study was conducted for the Survey and Analysis Division of the United States Environmental Protection Agency, Office of Pesticides and Toxic Substances (OPTS). The primary objective of this study was to determine, within the constraints of time and information availability, the quantity of 2-nitropropane released to the environment annually, the sources and locations of these releases and the form in which 2-nitropropane is released.

The information used to prepare this Level I materials balance was gathered by telephone inquiries and literature searches conducted by JRB staff personnel.

Many assumptions and estimations were made to account for all releases of 2-nitropropane to the environment. Assumptions for estimates are clearly stated and the results represent the best analysis of the currently available data.

The sources of 2-nitropropane and their associated releases are discussed in Section 2.0. Consumptive, nonconsumptive and miscellaneous uses and exports are discussed in Section 3.0. Releases of 2-nitropropane from the uses of nitromethane, nitroethane, and 1-nitropropane are discussed in Section 4.0. A summary of environmental releases of 2-nitropropane is presented in Section 5.0. Section 6.0 summarizes the releases that occur from the disposal and destruction of wastes containing 2-nitropropane, and Section 7.0 of the report identifies gaps in the available data.

2.0 ENVIRONMENTAL RELEASE ASSOCIATED WITH PRODUCTION OF 2-NITROPROPANE

During the manufacturing and processing of nitroparaffin, 2-nitropropane is released directly to the environment from various points in the production process. Natural production sources are not identifiable, and indirect sources do not contribute significantly to the total production. Imports of 2-nitropropane are believed to be less than 0.5 kkg per year.

2.1 Environmental Release Associated with Direct Production

IMC Chemical Groups, Inc. of the International Minerals and Chemical Corporation is the sole producer of 2-nitropropane in the United States. The annual production is estimated at 30 million pounds or 14,000 kkg (NIOSH 1977a). According to IMC, the actual production quantity of 2-nitropropane in 1979 was approximately equal to the estimated figure.*
U.S. International Trade Commission (1979) also listed IMC as the only producer of 2-nitropropane.

The 2-nitropropane production process is based on the vapor-phase nitration of propane with nitric acid (Shreve and Brink 1977). The main reaction involved in this process can be expressed as follows:

a Percent by weight

2-Nitropropane and other nitroparaffins and derivatives are produced at Sterlington, Louisiana. Figure 2.1 shows the location of the producer of 2-nitropropane.

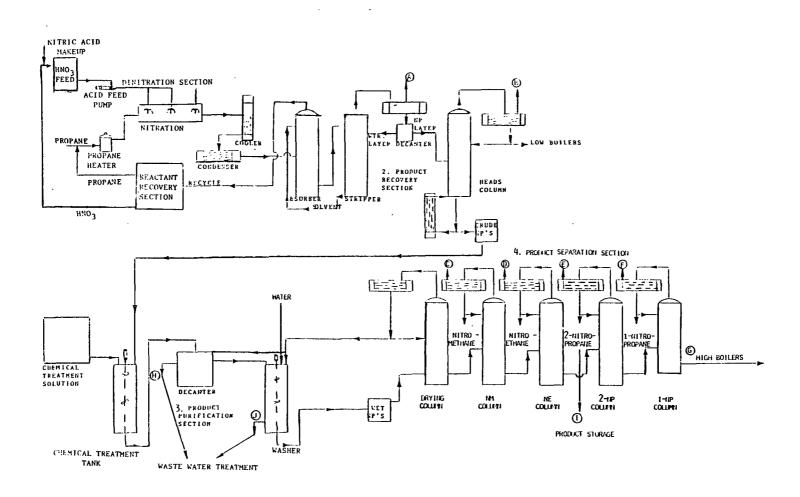
The production process of 2-nitropropane and other nitroparaffins involves the following steps: (1) vapor-phase nitration, (2) product recovery, (3) reactant recovery, (4) product purification, and (5) product separation (Reidel 1956). A simplified flow diagram of the production process is illustrated in Figure 2.2.

The vapor-phase nitration step consists of reacting propane gas with nitric acid at 400° F and 100 pisa in an adiabatic reactor employing nitric acid sprays. The gaseous products are then cooled, condensed, and

^{*}G. Hess, IMC: personal communication with P. Le, JRB Associates, January 1980.



Figure 2.1 Location of Producer of 2-Nitropropane



Source: Reidel 1956

Figure 2.2 Flow Diagram of the Production of 2-Nitropropane by the Direct Nitration Process

recovered in the second step. Cooled products, which consist of nitro-paraffins, water, excess propane, and nitrogen oxide, are separated by absorption and stripping. Excess propane and nitrogen oxide are scrubbed out by absorption and are sent to the reactant recovery section. The absorbed nitroparaffins are then stripped. The stripped paraffins may contain a small amount of low-boiling oxidation products such as ketones and aldehydes; these substances are then removed from the nitroparaffin stream as head products in the heads column (Reidel 1956).

In the product purification step, the nitroparaffins are chemically treated and then washed with water. Chemical treatment of the nitroparaffins is necessary since a small amount of impurities contained in the nitroparaffins makes them corrosive for ordinary carbon steel and unstable (Reidel 1956).

In the last step, products are separated by distillation. Here, the water-washed nitroparaffin products are first dried in a drying column. Then nitromethane, nitroethane, 2-nitropropane, and 1-nitropropane are successively recovered from the product stream by fractionation (Reidel 1956).

The following sections will discuss the environmental releases of 2-nitropropane from the production process.

2.1.1 Release of 2-Nitropropane to the Air from Process Vents

As shown in Figure 2.2, 2-nitropropane emissions to the air can occur from:

- The condenser for the nitrification process
- The stripper vent (Stream A)
- The light-end column vent (Stream B)
- The nitromethane distillation column vent (Stream C)
- The nitroethane distillation column vent (Stream D)
- The 2-nitropropane distillation column vent (Stream E)
- The 1-nitropropane distillation column vent (Stream F).
- (1) Condenser for the nitrification process. There is no information on the emission of 2-nitropropane from the condenser. This source is not believed to have a significant emission rate, since the condenser is only used as a container of the cooled product from the reactor. The only opening on a condenser is a safety valve which is only used in case of emergency. Thus the emission from the source does not greatly contribute to the total emission from process vents.
- (2) Stripper vent (Stream A). There is no information on the emission rate of 2-nitropropane from the stripper vent during direct nitration. Judging from engineering knowledge about this type of vent, we estimate that the typical emission rate of a stripper vent is 0.0005 kkg/kkg of product. The products generated from the stripper include

nitromethane, nitroethane, 2-nitropropane, and 1-nitropropane. We assume that only 1 percent of the total emission from the stripper vent is composed of 2-nitropropane because of the low volatility of this chemical. As shown in Section 2.1, 2-nitropropane product (14,000 kkg) represents 40 percent of the total nitroparaffins produced. Thus, the total quantity of nitroparaffins produced is 35,000 kkg. The uncontrolled emission of 2-nitropropane from Stream A can be calculated from the total production of nitroparaffins, the emission rate, and the fraction of 2-nitropropane in emissions as 0.18 kkg.

- (3) Light-end column (Stream B). Information on the quantity of 2-nitropropane released from the light-end column vent during direct nitration was not found in the literature. To complete the materials balance we estimated an emission rate from this source. The typical emission rate of a light-end column can vary from 0.0005 to 0.0015 kkg/kkg of product. Therefore, a typical emission rate of the light-end column vent would be approximately 0.001 kkg/kkg of product. The products produced from the distillation column are nitroparaffins. We also assume that 2-nitropropane is present at only 10 ppm, since this stream consists mainly of light-end materials such as aldehydes and ketones. The uncontrolled emission of 2-nitropropane from light-end column vents can be calculated from the total production of nitroparaffins, the emission rate, and the level of contamination as 3.5 x 10 kkg.
- (4) Nitromethane distillation column vent (Stream C). Nitromethane is separated from the mixed nitroparaffin crude stream by fractional distillation. We estimate the typical emission rate of a distillation vent at 0.001 kkg/kkg of nitromethane produced. As shown in Section 2.1, nitromethane constitutes 25 percent of the total quantity of nitroparaffins produced, or an estimated 8,750 kkg for 1979. This stream consists mostly of inert gas such as nitrogen and other volatile organic components (VOC). We assume that it is composed of 80 percent inert gas and 20 percent VOC because the main purpose of the distillation column vent is to release inert gases such as nitrogen and oxygen and to prevent internal pressure build-up. We estimate that only 0.1 percent of the total VOC is 2-nitropropane due to the low volatility of this compound. Therefore, the proportion of 2-nitropropane in the gas stream released from the distillation column vent is 0.02 percent. Based on these assumptions, the uncontrolled emişsion of 2-nitropropane from this source can be estimated at 1.8 x 10^{-3} kkg.
- (5) Nitroethane distillation column vent (Stream D). In the product separation unit shown in Figure 2.2, nitroethane is also removed from the crude nitroparaffin stream by fractional distillation. Information on the amount of 2-nitropropane emitted from the nitroethane distillation column was not found in the literature. As discussed in Section (4) above, we estimate that the typical release rate of a distillation column vent is approximately 0.001 kkg/kkg of nitroethane. Nitroethane comprises about 10 percent of nitroparaffins produced (Section 2.1), or 3,500 kkg in 1979. We also assume that the fraction of VOC in the released gas stream is about 20 percent. Of the total VOC, we estimate that 3 percent is 2-nitropropane. This percentage is based on the fact that nitroethane cannot be effectively separated from 2-nitropropane since the boiling

temperature difference between these two compounds is rather small (6° C); the nitroethane product contains 3 to 4 percent 2-nitropropane by weight (Riddick and Bunger 1970). Therefore, the concentration of 2-nitropropane in the released gas stream is estimated at 0.6 percent. Based on the above information, the uncontrolled emission of 2-nitropropane from this source is estimated as 2.1×10^{-6} kkg.

- (6) 2-Nitropropane distillation column vent (Stream E). 2-Nitropropane is removed from the crude nitroparaffin as an overhead product of the 2-nitropropane distillation column. Again, there is no information on the amount of 2-nitropropane released from the distillation vent. We assume again that the typical emission rate of a distillation column vent, 0.001 kkg/kkg of product, can be applied to this vent. We also estimate that VOC comprise 20 percent of the released gas stream. We speculate that 2-nitropropane constitutes 90 percent of the total VOC since this vent is located on the overhead stream of the 2-nitropropane distillation column. 2-Nitropropane therefore represents 18 percent of the constituents in the released gas stream. The uncontrolled emission of 2-nitropropane from the 2-nitropropane distillation column vent can then be estimated at 2.5 kkg.
- (7) 1-Nitropropane distillation column vent (Stream F). As shown in Figure 2.2, 1-nitropropane is the last compound removed from the crude nitroparaffin stream. In the absence of specific information, we assume that the gas stream released from the distillation column vent is approximately 0.001 kkg/kkg of 1-nitropropane. About 25 percent of nitroparaffin production is 1-nitropropane (Section 2.1); this amounts to 8,750 kkg for 1979. We also assume that VOC comprise 20 percent of the released gas stream. We estimate that 2-nitropropane constitutes 3 percent of the total VOC, since 2-nitropropane comprises 3 to 4 percent (by weight) of 1-nitropropane product (Riddick and Bunger 1970). Therefore, 2-nitropropane constitutes 0.6 percent of the released gas stream from this source. From these values, an uncontrolled emission figure of 5.3 x 10 kkg can be estimated.
- (8) Total uncontrolled and controlled releases. The total quantity of 2-nitropropane released directly to the air from all vents shown in Figure 2.2 is the sum of all uncontrolled emissions from these sources, or 2.8 kkg. According to IMC (Purdy 1977), all waste gases generated by the production process are controlled by incineration and according to IMC (1979), a properly designed incinerator could achieve a destruction efficiency of 90 percent or more. Therefore, the controlled emissions of 2-nitropropane from the production process vents is 0.3 kkg.
- 2.1.2 Emissions of 2-Nitropropane to Air from Product Storage Tanks (Stream I)

There are two kinds of emissions from storage tanks: loss due to tank breathing, and working loss or loss due to tank cleaning and filling. Emission factors for 2-nitropropane from "old" fixed roof tanks can be calculated as described in the AP-42 report (USEPA 1977b). The following sections discuss the emissions from storage tanks. The calculations are presented in the Appendix.

(1) Tank breathing. Tank breathing losses are defined by the USEPA as losses resulting because of the thermal expansion of existing vapors, vapor expansion as a result of barometric pressure changes, or added vaporization in the absence of a liquid-level drainage (USEPA 1977b).

The emission factor for 2-nitropropane lost from storage tanks due to tank breathing can be estimated using the method outlined in USEPA (1977b). The calculations associated with this estimate are shown in the Appendix. The following assumptions were made to estimate the emission of 2-nitropropane due to tank breathing:

- 2-Nitropropane is stored in fixed roof tanks, and the tank is in "worn" condition
- All 2-nitropropane is stored for at least 1 day before it is distributed for other uses
- There are 300 working days in a year
- The ambient temperature is 20°C
- The tank volume is 15,000 gallons, the average tank height is 10 feet, and the diameter is 16 feet
- The production site has two similar tanks painted either white or aluminum
- Ambient temperature change from day to night is 15°F
- The liquid level inside the tank is half the average height of the tank.

Based on the above assumptions, the calculated emission factor is 6.7 x 10⁻⁴ kkg/day (see Appendix). The annual uncontrolled emission from product storage due to tank breathing can be estimated at 4.0 x 10⁻¹ kkg/year.

We then assume that emission of 2-nitropropane due to tank breathing is controlled by a refrigerated system. The typical efficiency range of such recovery systems is 65 to 95 percent. Therefore, the estimated release rate is 20 percent. The controlled emission can then be estimated at 8.0×10^{-2} kkg.

- (2) Tank handling and cleaning. Environmental losses to air due to tank handling and cleaning are defined as working loss. The AP-42 report (USEPA 1977b) has also outlined the method for estimating working loss. The following assumptions are applicable for these calculations:
 - The ambient temperature is 20°C
 - The storage tank capacity is 15,000 gal
 - The crude oil factor is 1 (USEPA 1977b)
 - The production site has two storage tanks (15,000 gal).

The emission factor for working loss can then be estimated at 9.5×10^{-5} kkg/ 10^3 gal. The calculations associated with this estimate are presented in the Appendix. Based on an annual throughput volume of 2-nitropropane of 3.7×10^6 gal and the above emission factor, the uncontrolled emission of 2-nitropropane due to working loss is estimated as 7.0×10^{-6} kkg. Assuming that working losses of 2-nitropropane from product storage can be controlled by a vapor recovery system with a 20 percent release rate, then the controlled emissions are estimated at 1.4×10^{-6} kkg.

2.1.3 Emissions of 2-Nitropropane to Air from Fugitive Sources

Sources of fugitive emissions within the production plant include process pumps, compressors, process valves, and pressure relief devices. According to Hobbs and Stuewe (1979a), a plant that produces about 50,000 kkg of products per year typically has about 20 pumps, 400 valves, 2 compressors, and 15 pressure relief valves. Typical uncontrolled emission factors are 1.5 kg/day per pump seal; 0.068 kg/day per valve; 3.9 kg/day per compressor seal; and 1.1 kg/day per relief valve (Hobbs and Stuewe 1979b). The reported leakage frequency for pumps, compressors, and valves averages 10 percent per year (Hobbs and Stuewe 1979a). Assuming that there are 300 working days per year, the leakage frequency is 30 days per year. From this value and those for equipment numbers and release factors given above, the uncontrolled emissions from fugitive sources can be estimated as follows:

•	Pump seal leaking:			10 ⁻¹	_
•	Valve leaking:			10 ⁻¹	_
•	Compressor seal leaking:			10 ⁻¹	_
•	Pressure relief valve leaking:	5.0	x	10 ⁻¹	kkg.

The total amount of nitroparaffins in uncontrolled fugitive emissions is estimated at 2.5 kkg. Assuming that 40 percent of the nitroparaffins released to air is 2-nitropropane, then 1 kkg of 2-nitropropane is released uncontrolled as fugitive emissions. If 90 percent of fugitive emission sources can be controlled by regular maintenance procedures and quick response to and repair of leaks, then the controlled emissions of 2-nitropropane from fugitive sources are estimated at 0.1 kkg.

2.1.4 Release of 2-Nitropropane to Air and Water During Waste Water Treatment

There is no information on the quantity of 2-nitropropane released to water from the direct nitration process. As shown in Figure 2.2, potential sources of waste water containing 2-nitropropane are the decanter and the water wash unit (streams H and J). Calculation of a waste water emission factor for 2-nitropropane is based on the following assumptions:

• The average density of the mixed nitroparaffin stream is estimated at 1.1 kg/ ℓ .

- The volume of water used to wash the chemically treated nitroparaffin is equal to the volume of nitroparaffins produced.
- The drying column can separate out all the water in the wet nitroparaffin stream, and the separated water stream is recycled to the water wash unit for further use.
- Of the recycled water stream from the drying column, 10 percent is reintroduced to the drying column as reflux stream, and the rest is recycled to the water wash unit.
- Of the remaining 90 percent of the recycled water stream, 80 percent is reused as process water and 20 percent is discarded as waste water; thus, the amount discarded is 18 percent of the total water used.
- Maximum solubility of 2-nitropropane in water occurs during the wash phase (1.7 ml/100 ml at 20°C).
- A negligible amount of 2-nitropropane is lost from the decanter.
- There is no recovery of the nitroparaffins discharged to water from the wash unit.

As calculated in Section 2.1.1, the total quantity of nitroparaffins produced in 1979 is estimated at 35,000 kkg; thus, the total volume of nitroparaffins produced is 3.2×10^{-2} . The total volume of water used in the water wash unit is also 3.2×10^{-2} , and the volume of water discharged to waste water treatment is 5.8×10^{-2} or 18 percent of the total volume of water used. The amount of 2-nitropropane in the discharged waste water is then estimated at 9.9×10^{-2} ml, or 9.9×10^{-2} . From the density of 2-nitropropane (0.992 kg/l) the total quantity of 2-nitropropane emitted to waste water treatment is calculated as 9.8×10^{-2} kg, or 9.8×10^{-2} kg.

2-Nitropropane is degraded by microbial action during waste water treatment. The enzymatic reactions responsible for degradation are believed to be similar to those studied in higher organisms. Little (1957) demonstrated the degradation of 2-nitropropane by extracts of Neurospora crassa and pea seedlings. The enzymatic reaction is an oxidative denitrification yielding nitrite and carbonyl compounds; nitrite is further metabolized to ammonia via other reactions. The oxidative degradation of 2-nitropropane can be represented by the following reaction:

$$2 \text{ CH}_3 \text{CH(NO}_2) \text{CH}_3 + \text{O}_2 \longrightarrow 2 \text{ CH}_3 \text{COCH}_3 + 2 \text{ HNO}_2$$

Kido et al. (1976) identified the enzyme responsible for catalyzing this reaction as a dioxygenase. Dioxygenases are defined as enzymes catalyzing reactions in which both atoms of the oxygen molecule are incorporated into the substrates. Kido suggested that the oxidative degradation of 2-nitropropane is very rapid under conditions of maximal temperature (20° to 40° C) and pH (6.8 to 7.0).

We assume that 90 percent of the 2-nitropropane in waste water is biodegraded during the waste water treatment cycle. Because aeration of the waste water is part of the treatment process, loss of 2-nitropropane to air can be anticipated; we assume that this emission constitutes 9 percent of the 2-nitropropane present in the influent of treatment facilities. The remaining 1 percent is assumed to remain in the treated water effluent. (These percentages are only estimates and should be verified in later studies.) From these percentages, we estimate that in 1979, 9 kkg of 2-nitropropane were lost to air, 88 kkg were biodegraded, and 1 kkg was retained in the water effluent. According to IMC (Purdy 1977), the waste water containing nitrate and acids is then discharged by deep-well injection.

2.1.5 Emission of 2-Nitropropane to Air During Heavy-End Waste Disposal

Heavy-end wastes containing 2-nitropropane can be generated from the 1-nitropropane distillation column. These are typically disposed of through incineration. There is no information on the quantity of 2-nitropropane released in this manner. We estimated the quantity of 2-nitropropane generated by use of the following assumptions:

- The emission factor for this process is the typical factor for heavy-end waste from a distillation column, 0.1 kkg/kkg of product.
- 2-Nitropropane comprises 10 percent of the heavy-end waste stream since the overhead product (mainly 1-nitropropane) is 3 to 4 percent 2-nitropropane by weight.

Therefore, the emission factor for 2-nitropropane in the heavy-end waste is 0.01 kkg/kkg of 1-nitropropane produced. The quantity of 1-nitropropane produced in 1979 is estimated at 8,750 kkg. Thus, the quantity of 2-nitropropane contained in heavy-end wastes is estimated at 87.5 kkg.

Heavy-end wastes may contain toxic substances, and current methods of hazardous waste disposal usually require incineration. Thus, we assume that the heavy-end waste generated from this source is incinerated. We also assume that the incinerator used to dispose of heavy-end wastes can achieve a 90 percent efficiency. Then the amount of 2-nitropropane released to air from the incinerator can be estimated at 8.8 kkg. The quantity of 2-nitropropane remaining in the ash discharged by the incinerator is estimated to be negligible.

2.1.6 Emissions of 2-Nitropropane During Loading and Shipping

According to NIOSH (1977), 96 to 98 percent of 2-nitropropane is shipped by tank cars and trucks. It is assumed that this percentage applies to the portion of 2-nitropropane production that is used nonconsumptively, 5,600 kkg and to exports, 1,400 kkg.

According to USEPA (1977b), there are two kinds of emissions during shipping of liquid products: loading and transit losses. The principal methods of loading cargo carriers are the splash loading method, in which the fill pipe dispensing the liquid product is only partially lowered into

the tank, and the submerged loading method, in which the fill pipe is lowered almost to the bottom of the tank or enters the tank from the bottom. Either type of loading results in high levels of vapor generation and loss.

Transit losses are much smaller than those during loading. Small quantities of vapor are lost due to temperature and barometric pressure changes during transportation.

Releases of 2-nitropropane during loading and shipping in 1979 were estimated as 0.8 kkg. The calculations are shown in Appendix B.

Other processes during which fugitive releases could occur include taking quality control samples, drumming, and spills during loading (NIOSH 1977). JRB concluded that releases from these sources are insignificant compared to those from other sources.

Figure 2.3 is a flow diagram showing a summary of environmental releases of 2-nitropropane from the direct nitration process.

2.2 Releases of 2-Nitropropane Associated with Inadvertent Production Sources

Information on the indirect production of 2-nitropropane from other chemical production processes was not found in the literature. It seems unlikely that 2-nitropropane can be produced indirectly because the chemical can only be formed under the following conditions:

- The presence of a source of propane, or at least a source of hydrocarbons
- The presence of a source of nitric acid
- A reaction temperature of approximately 400°F
- A reaction pressure of approximately 100 psia
- Vapor-phase reaction conditions.

In our literature search we did not find many chemical production processes that use both propane and nitric acid as materials and also operate at high temperature and pressure. Some chemical reactions, such as that of silver nitrite with an alkyl halide (Riddick and Bunger 1970), can produce 2-nitropropane inadvertently as a by-product, but we believe that these reactions do not occur in sufficient quantity to merit further consideration as a potential source of 2-nitropropane production. Therefore, as judged from the information available, we believe that inadvertent production sources do not significantly contribute to the total production of 2-nitropropane.

2.3 Release of 2-Nitropropane Associated with Natural Production Sources

During the course of data gathering and analysis, no information was found on the formation of 2-nitropropane from natural sources. We

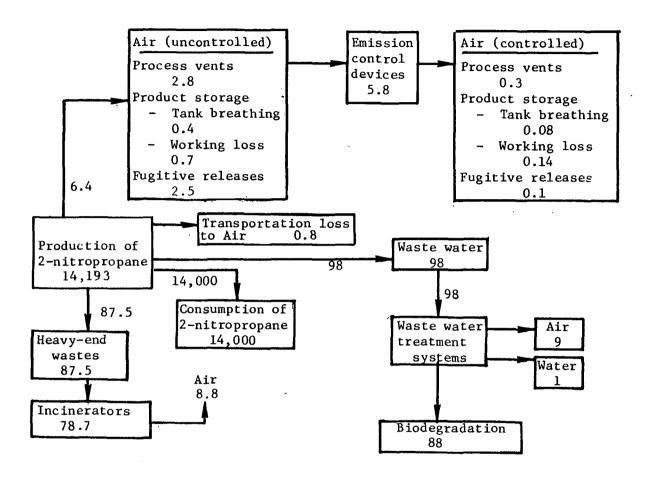


Figure 2.3 Environmental Releases of 2-Nitropropane During its Production (kkg)

concluded that 2-nitropropane cannot be produced naturally, since the critical conditions for formation, such as temperature, pressure, and the coexistence of propane and nitric acid, are not met concurrently.

2.4 Imports

According to information provided by the Chemical Information Division, USEPA, 2-nitropropane is probably imported by Thorson Chemical Corporation, New York, in quantities of less than 0.5 kkg per year (USEPA 1979b).

3.0 ENVIRONMENTAL RELEASE DURING THE USES OF 2-NITROPROPANE

The annual consumption of 2-nitropropane is estimated at 14,000 kkg (NIOSH 1977). Of this amount, 7,000 kkg are believed to be used by the producer for the production of other chemicals, 5,600 kkg are sold domestically (NIOSH 1977), and 1,400 kkg are exported.*

3.1 Release of 2-Nitropropane Associated with the Production of Chemicals

The following chemicals are synthesized from 2-nitropropane: 2-nitro-2-methyl-l-propanol; 2-amino-2-methyl-l-propanol; 2-amino-2-ethyl-1,3-propanediol; 2-amino-2-methyl-1,3-propanediol; and 2-amino-2-hydroxymethyl-1,3-propanediol (USITC 1978).

3.1.1 Release of 2-Nitropropane Associated with Production of 2-Nitro-2-Methyl-1-Propanol

2-Nitro-2-methyl-1-propanol can be produced by the reaction of 2nitropropane with formaldehyde, as follows:

2-nitropropane formaldehyde 2-nitro-2-methyl-1-propanol

Figure 3.1 is a flow diagram showing the process for preparation of 2-nitro-2-methyl-1-propanol and 2-amino-2-methyl-1-propanol.

According to IMC, the quantity of 2-nitropropane used in the production of 2-nitro-2-methyl-1-propanol is approximately 20,000 lb/day (or 9.1 kkg/day) (Purdy 1977). The typical number of working days per year for a chemical plant is about 300, but actual working days can fluctuate from 260 to 350. Assuming that the IMC production plant operates 300 days per year, the total quantity of 2-nitropropane consumed in the production of 2-nitro-2-methyl-1-propanol can be calculated at 2,700 kkg.

To calculate the quantity of 2-nitro-2-methyl-1-propanol produced from the reaction of 2-nitropropane with formaldehyde, we assume that the overall yield of this reaction is 80 mole percent. This assumption is based on the reaction yield range of 70 to 90 percent necessary if an industrial chemical process is to be economically feasible. The estimated amount of 2-nitro-2-methyl-1-propanol produced in 1979 was 2,900 kkg.

(1) Release of 2-nitropropane to air from process vents. As shown in Figure 3.1, a possible source of air emission is the concentration still

^{*}G. Hess, IMC: personal communication with P. Le, JRB Associates, January 1980.

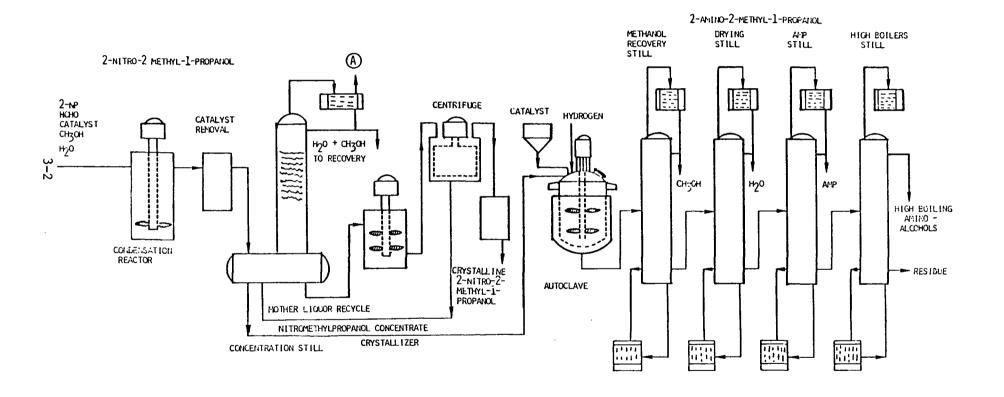


Figure 3.1 Flow Diagram for the Production of 2-Nitro-2-Methyl-1-Propanol and 2-Amino-2-Methyl-1-Propanol Source: Reidel 1956

vent (stream A). Since there is no information on environmental emissions of 2-nitropropane from this production process, we estimate that the emission rate from this vent is 0.001 kkg/kkg of product, a rate typical for a distillation column. Since most 2-nitropropane is reacted to produce 2-nitro-2-methyl-1-propanol, 2-nitropropane would occur only as an impurity in the emission stream. The level of 2-nitropropane contamination in this stream is estimated at 50 ppm with a range of 100 to 1 ppm. Based on these assumptions, the quantity of 2-nitropropane released to air uncontrolled from this source is estimated at 1.5×10^{-4} kkg.

Assuming that this emission source can be controlled by incineration at 90 percent efficiency, then the controlled emission of 2-nitropropane from the concentration still vent can be calculated as 1.5 x 10 kkg.

- (2) Emission to water. Information on the waterborne emission of 2-nitropropane from production of 2-nitro-2-methyl-1-propanol was not found in the literature. An analysis of the production process did not reveal any possible source of emission to water. Therefore, we assume that during the formulation of 2-nitro-2-methyl-1-propanol, emission of 2-nitropropane to water is insignificant.
- (3) Emission to land. Again, there is no information available on land-destined emissions from the production process of 2-nitro-2-methyl-1-propanol. After examination of the manufacturing process, we conclude that the only possible source of emission to land occurs in the catalyst removal section of the process. There is no information on the type and amount of catalyst used in this process, but we believe that either potassium hydroxide or manganese bromide is used.

The common practice for disposal of spent catalysts is to store the waste in 55-gallon drums that are disposed in landfills. Since we have no information on the type or amount of catalyst used, we cannot quantify the 2-nitropropane released from the land-destined wasted catalyst.

3.1.2 Release of 2-Nitropropene During the Uses of 2-Nitro-2-Methyl-1-Propanol

As discussed in Section 3.1.1, the quantity of 2-nitro-2-methyl-1-propanol produced is estimated at 2,900 kkg. The level of 2-nitropropane contamination in 2-nitro-2-methyl-1-propanol is estimated at 50 ppm. Thus the total quantity of 2-nitropropane present in 2-nitro-2-methyl-1-propanol is estimated at 0.15 kkg.

2-Nitro-2-methyl-1-propanol is chiefly used to produce 2-amino-2-methyl-1-propanol. Other uses of 2-nitro-2-methyl-1-propanol are unknown. According to Reidel (1956), the 2-nitro-2-methyl-1-propanol final product is in crystalline form; thus, any contamination by 2-nitropropane is considered negligible. The rationale for this assumption is that during further purification of 2-nitro-2-methyl-1-propanol by the crystallization method, any liquid contaminant such as 2-nitropropane is efficiently removed from the final product.

The production process for 2-amino-2-methyl-1-propanol from 2-nitro-2-methyl-1-propanol was shown in Figure 3.1. 2-Amino-2-methyl-1-propanol can be used in the synthesis of surface agents, vulcanization accelerators, and pharmaceutical products. It can also be used as an emulsifying agent for cosmetic creams and lotions, mineral oil and paraffin waxes, leather dressings, textile specialties, polishes, and cleaning compounds (Merck 1976).

Assuming that 90 percent of 2-nitro-2-methyl-1-propanol is used for the production of 2-amino-2-methyl-1-propanol, then the quantity of 2-nitropropane introduced into the amino alcohol production is 0.13 kkg. We assumed that during this production process, 99 percent of contaminant 2-nitropropane (0.13 kkg) is removed from the product; the remaining 0.001 kkg is assumed to be contained in the product. We think that this level of contamination is not high enough to justify further consideration.

3.1.3 Release of 2-Nitropropane During Formulation and Uses of Aminohydroxy Compounds

As mentioned in Section 3.1, 2-nitropropane is used to produce amino-hydroxy compounds in addition to 2-nitro-2-methyl-1-propanol. The uses of some major aminohydroxy compounds potentially derived from 2-nitropropane were listed in the Merck Index (1976). 2-Amino-2-ethyl-1,3-propanediol and 2-amino-2-methyl-1,3-propanediol can be used in the synthesis of surface-active agents, vulcanization accelerators, and pharmaceuticals, as emulsifying agents, and as absorbents for acidic gases such as carbon dioxide or hydrogen sulfide. Information pertaining to the production of these compounds was not found in the literature.

According to IMC,* the total quantity of 2-nitropropane consumed captively in-plant is estimated at 7,000 kkg, which includes 2,700 kkg used for the production of 2-nitro-2-methyl-1-propanol. Therefore, 4,300 kkg of 2-nitropropane were consumed in the production of other aminohydroxy compounds. We have no information on the production processes of these aminohydroxy compounds; therefore, we cannot quantify any releases of 2-nitropropane from their production or use. We believe that the level of contamination of 2-nitropropane in the aminohydroxy compounds is so low that it does not contribute significantly to the total release of 2-nitropropane to the environment.

3.2 Release of 2-Nitropropane Associated with Nonconsumptive Uses

Of the 14,000 kkg of 2-nitropropane produced in the United States in 1977, nonconsumptive uses accounted for 5,600 kkg of the total amount produced. The major nonconsumptive uses were determined to be printing inks and surface coatings. Minor uses of 2-nitropropane were for explosives, rocket propellants, adhesives, gasoline additives, dyes, pesticides, rubber, and chemical reactions.

^{*}G. Hess, IMC: personal communication with P. Le, JRB Associates, January 1980.

The following sections detail the amounts of 2-nitropropane used in each area identified, and the amounts of multimedia emissions (to air, water, and land) associated with each.

3.2.1 Printing Inks

A major use for 2-nitropropane is as a solvent in printing inks (NIOSH 1977). Printing inks can be classified into four categories: letterpress, lithographic, flexographic, and gravure. Letterpress and lithographic printing inks are viscous, tacky pastes with low solvent concentrations. Flexographic and gravure printing inks have low viscosity and high solvent concentrations. 2-Nitropropane cannot be used in letterpress and lithographic printing inks, but it can be used in flexographic and gravure printing inks.*

Even though 2-nitropropane is reported to be used in flexographic and gravure printing inks, the literature contains scant information on the quantities of 2-nitropropane utilized for this purpose. The IMC Company, sole producer of 2-nitropropane, refused to disclose any information. Therefore, JRB obtained data through telephone inquiries to trade associations, printing ink distributors, and manufacturers on use of 2-nitropropane in printing inks and the associated environmental releases.

The quantity of 2-nitropropane sold domestically for all uses in 1979 was estimated at 5,600 kkg. According to an industrial source, the quantity of 2-nitropropane used in printing ink is estimated at 50 percent of total usage, or 2,800 kkg.

The amounts of flexographic and gravure printing inks produced in 1979 were 70,000 and 143,000 kkg, respectively. A number of solvents are used in these inks. Telephone inquiries to printing ink distributors and manufacturers revealed that 15 percent of the flexographic and gravure printing inks contain 2-nitropropane as a solvent. Furthermore, a typical batch of flexographic printing ink containing 2-nitropropane as a solvent was estimated to contain 2 to 4 percent (by weight) of 2-nitropropane. From this information, the quantity of 2-nitropropane used in flexographic printing ink in 1979 was estimated at 210 to 420 kkg. 2-Nitropropane was also estimated to comprise less than 0.5 percent of the total quantity of flexographic ink produced. This estimate yields a value of 350 kkg of 2-nitropropane in flexographic ink. JRB has used this figure as its estimated of 2-nitropropane used in flexographic printing ink.

A typical batch of gravure printing ink using 2-nitropropane as solvent contains approximately 10 to 15 percent (by weight) of 2-nitropropane.† Thus, 2-nitropropane content in gravure printing inks is

^{*}D. Tuttle, consultant, Cranford, N.J.: personal communication with P. Le, JRB Associates, September 1980.

[†]Import Chemical Co., General Printing Ink Co., CPW Printing Co., Croda Ink Co., Converters Ink Co.: personal communications with E. Harrison, JRB Associates, January 1980.

[§]T. Bart, Inmont Corp.: personal communication with P. Le, JRB Associates, September 1980.

estimated at 2,150 to 3,220 kkg (average 2,680 kkg). Therefore, a second estimate for the total quantity of 2-nitropropane used in flexographic and gravure inks is calculated at 3,030 kkg. The average of the two estimates for 2-nitropropane used as a solvent in flexographic and gravure printing inks is 2,900 kkg.

(1) Releases of 2-nitropropane during formulation of printing inks. The manufacture of most kinds of printing ink can be resolved into two different stages: mixing and milling. In the mixing stage, the pigment, the vehicle, and dryers are mixed together thoroughly until the pigment is no longer discernible as a dry powder (Bowles 1961). In some cases, the mixture is heated to facilitate mixing. This is accomplished by use of high-speed mixers or ball mills (USEPA 1979c). Most inks are made in a batch process in tubs ranging in capacity from 5 to 1,000 gallons (USEPA 1979c). Figure 3.2 shows typical mixing machines used by the printing ink industry.

For low viscosity mixing, which includes preparation of gravure and flexographic printing inks, the mixing mechanism can be an impeller rotating at high speed or rotating blades sweeping the whole area of the mixer (Bowles 1961). When volatile liquids are used as solvents, covers are required through which the components can be added. Part (a) of Figure 3.3 shows a typical machine used for mixing flexographic and gravure printing ink.

To meet the required specifications, many inks may need additional dispersion through further milling processes. Milling can be accomplished with three-roll mills, sand mills, or ball mills.

(a) Releases of 2-nitropropane to air. Solvents used in printing ink, such as 2-nitropropane, can be released to air during the heating and mixing process. According to USEPA (1977b), the typical release rate for general organic solvents during the manufacture of printing ink is 60 kg/kkg of product. The amount of flexographic printing ink containing 2-nitropropane is estimated at 10,500 kkg. The percentage of 2-nitropropane used in flexographic ink is low: about 3 percent (by weight) of ink, or 5 percent (by weight) of solvents used. The latter value is calculated by assuming that solvents comprise 70 to 75 percent of solvent-based flexographic ink (Bowles 1961). We then assume that 2-nitropropane accounts for 5 percent of emitted solvents. Therefore, the calculated release rate for 2-nitropropane during the manufacture of flexographic printing ink is 3 kg/kkg of product; this gives an estimated release of 32 kkg to air from this manufacturing process in 1979.

The amount of gravure printing ink containing 2-nitropropane as solvent is 21,500 kkg (15 percent of the total quantity produced). These inks contain an average of 12.5 percent of 2-nitropropane (by weight). According to Bowles (1961), gravure inks consist of 50 to 60 percent solvents. Therefore, 2-nitropropane comprises 23 percent of total solvents in these inks. The release rate for 2-nitropropane is calculated as 23 percent of the solvent release rate of 60 kg/kkg reported by USEPA (1977b), or 13.8 kg/kkg of product. Therefore, the quantity of 2-nitropropane released to air during the production of gravure printing ink in 1979 was 296 kkg.

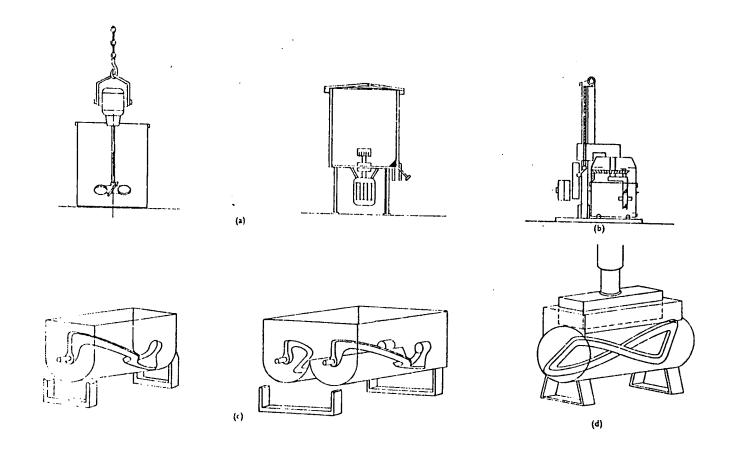


Figure 3.2 Types of Ink-Mixing Plants Source: Bowles 1961

The total quantity of 2-nitropropane released to air during the manufacture of printing ink in 1979 is estimated as 330 kkg, or 11 percent of the 2-nitropropane used in printing ink.

(b) Releases of 2-nitropropane to water. During the production of printing ink, the major source of water release of 2-nitropropane may come from the cleaning of mixing tubs. The ink industry commonly uses solvent, caustic, or water washes to clean ink tubs (USEPA 1979c).

The solvent wash technique is used extensively in cleaning tubs used to mix solvent-based and oil-based inks. In this process, there is virtually no discharge of waste water, since most solvents are recycled and recovered (USEPA 1979c). Caustic wash followed by water wash can sometimes be used to clean tubs from solvent-based inks.

According to USEPA (1979c), about 38 percent of the ink industry uses solvent wash techniques, 12 percent uses caustic wash techniques, and about 38 percent uses techniques that results in waste water discharge. For production of solvent-based printing inks, JRB estimated that about 56 percent of the plants use cleaning techniques that have no waste water discharge and 44 percent use cleaning methods that results in waste water releases (USEPA 1979c).

To calculate the amount of 2-nitropropane released to waste water during the production of printing ink, we assume that only 1 percent of the ink remains in the tub for cleaning. Using this assumption, the amount of 2-nitropropane lost during cleaning is estimated at 29 kkg. Of this amount, we assume that 56 percent (or 16 kkg) is not discharged to waste water, and the remaining 13 kkg is discharged to waste water.

The methods of waste water disposal for printing ink plants are reported by USEPA (1979c) and are presented in Table 3.1. According to this table, the amount of 2-nitropropane discharged is as follows: 4 kkg to POTWs, 1.7 kkg reused, 0.5 kkg landfilled, 3.5 kkg disposed by contractors, and 3.3 kkg disposed by other methods.

Of the quantity discharged to POTWs, we assume that 100 percent is destroyed by the slow process of biodegradation using activated sludge.

(2) Releases of 2-nitropropane resulting from its use as a printing ink solvent. The total amount of 2-nitropropane remaining in printing inks as solvent is 2,540 kkg. Flexographic and gravure printing applications fall into three major categories: publications, packaging, and specialties. In flexographic printing, the image areas are raised above the nonimage surface. A feed cylinder rotates in a trough of ink and delivers ink to the plate cylinder through a distribution roll (Vincent and Vatavuk 1978). Figure 3.3 shows a typical ink distribution system for flexography.

With the gravure printing method, image areas are recessed relative to nonimage areas. The gravure cylinder rotates in an ink trough, and excess ink is removed by a steel doctor blade. The ink in the cells is then transferred to the web when it is pressed against the cylinder by a rubber-covered impression roll, as shown in Figure 3.4 (Vincent and Vatavuk

Table 3.1 Waste Water Disposal Methods for Printing Ink Manufacture

Disposal method*		plants Percent of total	Plants using Number of plants	g water rinse Percent of total
Complete reuse	14	3.0	9	5.7
Partial reuse	45	9.8	18	11.4
Evaporation	34.	7.4	9	5.7
Discharge to city sewer	138	30.0	75	47.5
Discharge to storm sewer	13	2.8	5	3.2
Discharge to receiving stream	4	0.9	2	1.3
Impoundment on plant property	14	3.0	10	6.3
Incineration	2	0.4	1	0.6
Contract hauling	123	26.7	61	97.0
Landfilled	18	3.9	10	6.3
Well or septic tank	1	0.2		0

Source: USEPA 1979c

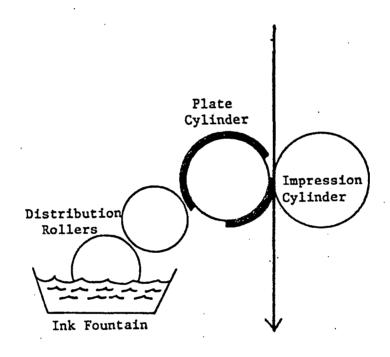
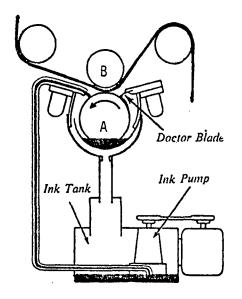


Figure 3.3 Ink Distribution System for Flexography Source: Vincent and Vatavuk 1978



- (A) (B) Etched cylinder Impression cylinder

Figure 3.4 Rotogravure Ink System Source: Vincent and Vatavuk, 1978

1978). According to Carpenter et al. (1975), about 90 percent of the applied solvent is believed to be driven out by evaporation during or after printing. The remaining 10 percent of the original solvent evaporates slowly from the solidified vehicle resins on the cool web.

Using the above data, JRB assumes that 100 percent (or 2,540 kkg) of the 2-nitropropane used in printing ink is released to air during the printing process.

To control the releases of hazardous chemicals used as solvents in printing ink, the printing industry uses vapor control techniques such as an activated carbon absorption system (Carpenter et al. 1975), and scrubbers. Assuming that these various control techniques can achieve a 90 percent efficiency, the remaining 2-nitropropane (254 kkg) is released to the air from use of printing inks containing 2-nitropropane.

If scrubbers are used to control the evaporation of 2-nitropropane during application of printing inks, JRB assumes that the scrubbing solution containing the 2-nitropropane will be discharged to a waste water treatment system where the 2-nitropropane can be biodegraded slowly. If an activated carbon system is used to control the emissions of vapor from the printing process, 2-nitropropane and other solvents will be recovered after the exhausted activated carbon is regenerated. The recovered product usually will be hauled for final disposal by contractors.

Figure 3.5 is a flow diagram of the environmental releases of 2-nitropropane during the production and uses of printing ink.

3.2.2 Surface Coatings

Coatings are used to protect and decorate various surfaces. Most coatings are composed of three ingredients: a binder, the pigment, and a volatile thinner or solvent. Binders are usually organic polymers that form a film which adheres to the substance being coated and binds the pigment particles. Pigments give color, opacity, and various other properties to the film. Thinners or solvents, which evaporate after application, make it possible to apply the coating. Because of its solubility in alcohol, the wide range of resins which it dissolves, and the low viscosity and evaporation rates of the resulting solutions, 2-nitropropane is used as a solvent in the formulation of vinyl, epoxy, cellulose, and other surface coatings (Kirk-Othmer 1964).

About 1,600 kkg of 2-nitropropane were in surface coatings in 1977; this estimate is derived in part (2) of this section. Almost all of this material, about 1,584 kkg, is believed to be released to air; this constitutes one of the largest estimated environmental releases of 2-nitropropane.

(1) Types of surface coatings.

(a) Vinyl. Vinyl surface coatings contain a vinyl resin as the basis of the coating binder. The resins are produced by emulsion, solution, suspension, or bulk polymerization techniques. They are used for their

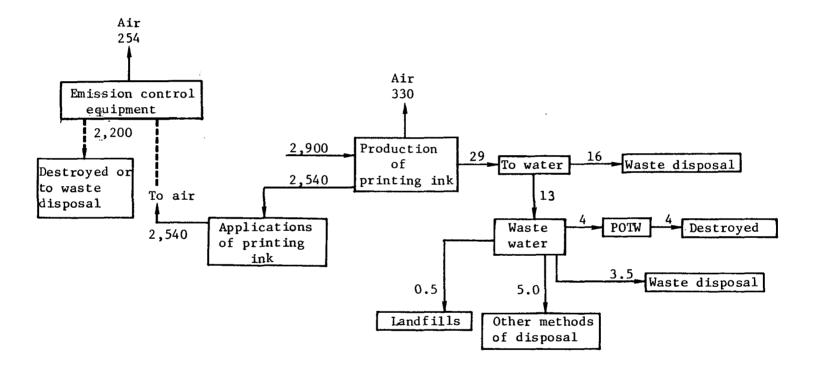


Figure 3.5 Flow Diagram of Environmental Release of 2-Nitropropane During the Production and Uses of Printing Ink

chemical resistance, water resistance, durability, fire retardant properties, lack of odor or taste, low cost, and versatility (SRI 1977). Although these vinyl resins are not very soluble in 2-nitropropane or hydrocarbons alone, they are readily soluble in latent solvent systems such as a combined 2-nitropropane-hydrocarbon solvent (Bennett 1979). These combined solvent systems also form azeotropic mixtures which enhance solvent release (evaporation) during application, thus producing a higher density film and improved adhesion. Such solvent-based coatings, formulated with a solvent instead of a water base, are known as lacquers. Polyvinyl acetate (PVAc), derivatives of PVAc, and polyvinyl chloride (PVC) are the major types of vinyl resins produced. Major applications for these vinyl surface coatings include latex house paints, flat wall paints, and industrial finishes such as metal container coatings. Approximately 1,500 paint companies are capable of producing vinyl surface coatings (SRI 1977).

(b) Epoxy. 2-Nitropropane is also used in epoxy surface coatings. These chemically resistant and electrical-grade coatings account for a substantial portion of the production volume of solid and liquid epoxy resins. They are primarily used for coating laboratory furniture, lawn furniture, appliances, hardware, magnetic wire, can and drum linings, military aircraft, and marine environments (docks, boats), and for floor coatings, masonry coatings, and swimming pool paints. Specialized formulations for automobile primers constitute the largest single market for epoxy resin coatings. Their advantages are superior heat resistance, toughness, and abrasion resistance. Disadvantages include high cost, poor color stability when exposed to ultraviolet radiation, and chalkiness after exposure to weathering (Mark and Gaylord 1969).

2-Nitropropane is probably used as a diluent during the formulation of epoxy surface coatings. The use of pine oil to reduce the viscosity of many epoxy resins has been documented (Mark and Gaylord 1969). Because pine oil is used in the same applications as 2-nitropropane, it is likely that 2-nitropropane is also used to reduce the viscosity of various epoxy resins. 2-Nitropropane may also be used in epoxy surface coating formulations (IMC 1979; NIOSH 1977) in azeotropic combination with hydrocarbons (such as butyl alcohol or toluene) which promote good solvent release and higher density epoxy coating (Bennett 1979).

(c) Cellulose. The use of 2-nitropropane in cellulose surface coatings was also studied. Either an organic or inorganic cellulose ester forms the base of these coatings. Nitroparaffins are used for dissolving commercial organic cellulose esters. Also, as with vinyl and epoxy coatings, 2-nitropropane may be used as an azeotrope to minimize the formation of moisture during the formulation and application of various lacquer surface coatings, especially plastic surface coatings. Of the three primary organic cellulose esters produced, cellulose acetate and cellulose acetate propionate are soluble or partially soluble in 2-nitropropane. Lacquers made from these cellulose esters serve as suitable protective coatings for wood furniture, paper, metal, glass, fabrics, and other plastics. They also serve as flexible substrates for foil, cellophane, and other packaging materials. Such lacquer surface coatings form by evaporative drying of organic solvents, as contrasted with polymerization of resin components or evaporation of water. Their primary

advantages are fast drying time and rapid hardening (Mark and Gaylord 1969). Major suppliers of cellulose lacquers for wood furniture include: Reliance Universal, Inc., Lilly Industrial Coatings, Inc., Guardsmen Chemicals, Inc., The Sherwin-Williams Co., Mobil Chemical Co./Chemical Coatings Division, and Inmont Corporation/Finishes Division, a major supplier of coatings for packaging materials (SRI 1977). Lacquers supplied by these companies may contain 2-nitropropane.

Use of 2-nitropropane in surface coatings made from inorganic cellulose ester (cellulose nitrate or nitrocellulose) has also been documented. Because of the solubility, viscosity in solution, compatibility with modifiers, and other physical properties of cellulose nitrate, its single largest use is as a surface coating. These coatings have a high film strength and rapidly release the solvent constituent. The solvent provides a means of dispersing and uniformly mixing the film components (SRI 1977). Nitrocellulose lacquers have many possible applications which include: topcoats for household and industrial furniture, radio and television cabinets, flooring, interior wood paneling, doors, bowling pins and alleys, broom handles, caskets, pencils, musical instruments, shoe heels, and toys and sporting goods; coatings for cellophane book covers, wallpaper, labels, menus, playing cards, and aluminum foil; primers and topcoats for aircraft, buses, house trailers, trucks, brass fixtures, and machine tools; leather finishes for shoes, table tops, luggage, and upholstery; fingernail polishes; household adhesives; and traffic paints (Kirk-Othmer 1964).

- (d) Paints. To ascertain whether 2-nitropropane is used in paints and, if possible, to quantify this usage, JRB contacted a number of companies from a list of probable 2-nitropropane users (NIOSH 1979). These companies included: Baltimore Copper and Paint Company, Baltimore, Maryland; El Paco Paint Company, Elkhart, Indiana; Dexter Corporation, Louisville, Kentucky; and the Porter Paint Company, Louisville, Kentucky. All of these companies stated that they do not use 2-nitropropane in paints. JRB assumes that the companies contacted reflect an accurate picture of the industry and concludes that 2-nitropropane has minimal, if any, use in nonlatex paints.
- (e) Chlorinated rubber surface coatings. No indication that 2-nitro-propane is a raw material for the formulation of chlorinated rubber surface coatings was found in a review of available literature (Kirk-Othmer 1964, Mark and Gaylord 1969) or in telephone conversations with industry officials.* Therefore, despite the statement that 2-nitropropane can be used as a solvent in the formulation of chlorinated rubber coatings (IMC 1980), it was assumed that 2-nitropropane is used in insignificant amounts for this purpose, if at all.
- (f) Other surface coatings. IMC literature (1979) reports many other potential uses of 2-nitropropane in manufacture of surface coatings, including elastomeric polyurethane, polystyrene, phenoxy resin, thermoplastic acrylic, alkyd resin, and thermoplastic polyamide systems.

^{*}K. Western, DuPont: personal communication with T. Shannon, JRB Associates, 1980.

However, during the course of literature investigations and telephone conversations about the surface coatings industry, we were unable to document the use of 2-nitropropane in the formulation of the above surface coatings. When we talked by phone with representatives of firms manufacturing 2-nitropropane-containing products, as listed in a NISOH (1979) data base, many contacts stated that the firms had either abandoned production of the product containing 2-nitropropane, or had stopped using 2-nitropropane in the product's manufacture. One industry official stated that, due to the possible carcinogenicity of 2-nitropropane, the product that required it has been taken off the market.* Therefore, we assumed that the use of 2-nitropropane during recent years in the formulation of the various surface coatings discussed above was insignificant.

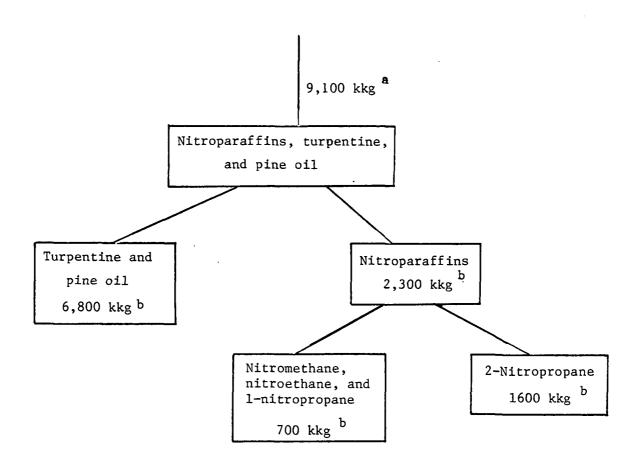
(2) Amount of use. Because of its chemical properties, 2-nitropropane is probably used in the formulation of cellulose, vinyl, and epoxy surface coatings. The present industrial trend towards replacement of chlorinated solvents is another factor that could add to the demand for 2-nitropropane. However, conversations with trade association representatives and industry officials did not yield any information on the amounts of 2-nitropropane used or its emissions to the environment.

An estimated 9,100 kkg of nitroparaffins, turpentine, and pine oil, the major solvents for surface coating formulation, were used in this industry in 1973. Due to the shift from solvent- to water-based coatings, no increase in the use of solvent-based coatings is expected through 1982 (SRI 1977). Therefore, it is assumed that 1979 total consumption of nitroparaffins, turpentine, and pine oil remained at 9,100 kkg. JRB has no data on the relative amounts of these solvents consumed in recent years. However, due to their low cost and ready availability, it is assumed that turpentine and pine oil constitute 75 percent of the 9,100 kkg consumed, or 6,800 kkg. The remaining 25 percent, or 2,300 kkg, is assumed to be nitroparaffins. About 70 percent of the total amount of nitroparaffins used in the surface coatings industry is believed to be 2-nitropropane. The amount of 2-nitropropane used by the industry is therefore estimated to be 1,600 kkg. The amounts of major solvents used in the surface coatings industry are summarized in Figure 3.6.

(3) Environmental releases of 2-nitropropane during the production of surface coating products. The manufacturing process for surface coating products generally consists of five steps: weighing, mixing, grinding, tinting and thinning, and packaging. There are no chemical reactions in these processes. A flow diagram of the surface coating manufacturing process is shown in Figure 3.7.

Weighing, assembling, and mixing of pigments and vehicles are the first steps in producing paint. The major ingredients such as resins, oils, and pigments are introduced into a feed tank in which they are weighed and then introduced into a mixer where they are thoroughly mixed. A conventional mixer is similar to a large dough kneader with a sawtooth

^{*}Mr. Young, Jones-Blair Co.: personal communication with T. Shannon, JRB Associates, 1980.



^a Source: SRI 1977

^b Source: JRB estimates

Figure 3.6 Usage of 2-Nitropropane and Other Solvents in the Surface Coating Industry

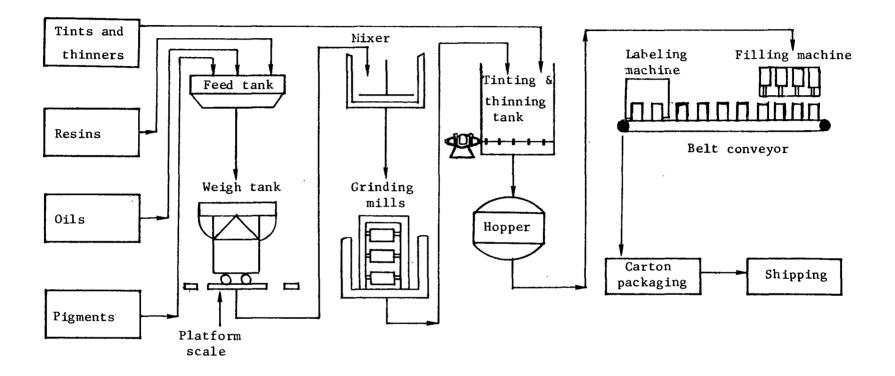


Figure 3.7 Flow Chart for the Mixing of Surface Coatings

blade. The batch is then ground and further mixed. Next, the paint is transferred to another section of the plant and thinned, generally with organic solvents, and tinted in agitator tanks. The paint is then transferred to the hopper of the filling machine and poured into cans (Shreve and Brink 1977; Handbook of Industrial Chemistry 1974; USEPA 1979c).

JRB believes that 2-nitropropane is probably used as a solvent for viscosity adjustment during the production of surface coatings. Therefore, it is probably added to the production process during the tinting and thinning phase.

The loss of organic solvents is usually estimated at 1 or 2 percent even under well-controlled conditions (USEPA 1977b). The total quantity of 2-nitropropane used for surface coating products is 1,600 kkg. By using an average loss factor of 1.5 percent, the 2-nitropropane lost to the air is estimated at 24 kkg.

As discussed in previous sections, 2-nitropropane is believed to be used mostly in the production of solvent-based surface coating products. The major source of solvent discharge into waste water (either treated or untreated) results from tank cleaning (USEPA 1979d). For most tanks used for formulating solvent-based surface coatings, solvent wash is a common method of cleaning. The caustic-wash technique also is used in some production plants (USEPA 1979d).

No direct discharges to waste water streams are believed to result from the solvent-wash cleaning technique. The solvents used for washing are usually recycled, reclaimed, reused, or sent to contractors for proper disposal (USEPA 1979d).

In plants using a caustic rinse system, the caustic residue is usually rinsed with water. In most caustic-wash systems, the caustic solution is recycled and reused. When the caustic solution is exhausted, it is properly stored in drums and sent to contractors for proper disposal (USEPA 1979d). The water used for rinsing off caustic residues is usually disposed as follows:

- Recycled into the caustic solution
- Drummed for hauling by contractors
- Discharged to either treated or untreated waste water streams.

According to USEPA (1979d), 60 percent of those plants specializing in solvent-based paints discharge no waste water; the remaining 40 percent are assumed to have direct waste water discharge. Because of this distribution, we assume that 40 percent of 2-nitropropane in residue cleaned from tanks is discharged in waste water.

During the production of surface coating products, 1 percent of the formulated products is assumed to remain in the tank before it is cleaned. For 1979, this quantity was 16 kkg. Of this residue, 40 percent (6.4 kkg)

is believed to be discharged to waste water treatment facilities, and the rest (9.6 kkg) is thought to be reused or drummed for contract hauling. The amount of 2-nitropropane remaining in the surface coating is 1,560 kkg.

According to IMC (1979), 2-nitropropane is biodegradable. Numerous organisms found in soil and in activated sludge slowly decompose it to carbon dioxide, nitrogen, and water. Therefore, the 2-nitropropane discharged to waste water is assumed to be totally biodegraded.

(4) Environmental releases of 2-nitropropane associated with the application of surface coating products. Surface coating can be applied in a variety of ways. Although architectural paints usually are applied by brush or roller, many applications are now done with spray equipment such as electrostatic spraying, hot spraying, steam spraying, two-component spraying, and aerosol spraying (Handbook of Industrial Chemistry 1974). Other application techniques include dipping, electrodeposition, flow coating, and powder coating. In dip application, objects to be coated are suspended and dipped into a large container of paint. Electrodeposition can be achieved by depositing coatings on a conductive surface from a water bath containing the paint (Handbook of Industrial Chemistry 1974). Some of the industries with surface coating operations are automobile assemblies, aircraft companies, container manufacturers, and furniture manufacturers (USEPA 1977b).

Releases of organic chemicals can occur during the application of surface coating products because of evaporation of the thinner and solvents used in formulating these coatings. Most of the solvents used in these products are emitted to the air during the application and drying of the coating. We thus assume that the total amount of 2-nitropropane in these products, 1,560 kkg, is released to the air after their application.

Figure 3.8 presents a flow diagram of the environmental releases of 2-nitropropane during the production and uses of surface coatings containing 2-nitropropane as solvent.

3.2.3 Miscellaneous Uses

(1) Adhesives. Until recently, adhesives were often selected arbitrarily. Wider use of adhesives in the last 30 years has prompted developments in the science of adhesives. Today, adhesives are an essential element in the manufacturing of many products, including building and household goods, shoe and leather products, automobiles, plywood, pressure-sensitive tapes, and corrugated cartons (Mark and Gaylord 1969).

Although JRB was unable to confirm the use of 2-nitropropane in adhesives,* the use of nitroethane and nitromethane, two other nitroparaffins, is documented. Organic solvents serve as good carriers and viscosity reducers for adhesive compositions. Contact cements and pressure-sensitive tapes are examples of cements utilizing organic solvents.

^{*}C. Witzman, National Starch Co.: personal communication with T. Shannon, JRB Associates, January 1980.

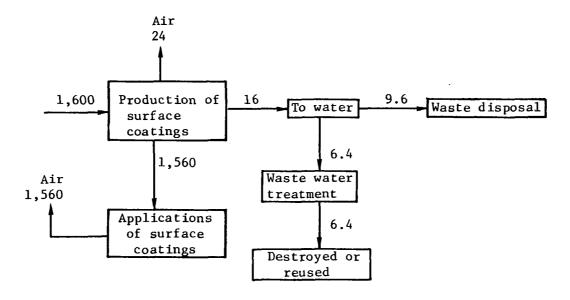


Figure 3.8 Environmental Release Flow Diagram of 2-Nitropropane During the Production and Uses of Surface Coatings

Simple polymer-containing and monomer-containing solvents are used in cements. Simple solvents, or blends of solvents, are selected for the bonding of a specific plastic. Solvency must be adequate to ensure sufficient flow during application, drying must complete without bloom, and a minimum of high-boiling residues must remain. The requirement for a solvent of lower boiling point would seem to indicate the use of nitroparaffins, which possess moderate boiling points. For bonding cellulose acetate, nitroethane is recommended, while nitromethane is recommended for the bonding of cellulose acetate butyrate and propionate (Mark and Gaylord 1969).

Although no quantitative data were obtained on use of 2-nitropropane in the adhesives industry, we believe that the use of 2-nitropropane in 1979 in this application could have been significant. Because of the extensive use of adhesives and the suitability of 2-nitropropane as a solvent in the industry, the extent of its use should be studied further.

(2) Explosives and rocket propellants. Use of 2-nitropropane in the explosives industry has been reported by an industry representative.* It is used in "prilling" formulations, in which 2-nitropropane and a 12 to 16 percent alcohol are mixed, yielding a high density, high energy-yielding explosive. Such a prill can be substituted for the traditional mixture of crushed ammonium nitrate, 6 percent fuel oil, and alcohol. The advantages of the 2-nitropropane prill are ease of formulation, good priming characteristics, and high detonation conduction. Disadvantages are its poor storage characteristics and higher cost. The market at present is not well established. Trojan, Inc., Philadelphia, was identified as a distributor, but this information could not be verified.

A representative of the Bureau of Explosives verified the use of 2-nitropropane in the explosives industry.† It is reportedly used as a prill, solely by IMC, Inc. Vulcan Materials, Inc. was suggested as a marketing agent for explosives containing 2-nitropropane. However, conversations with officials of both the Birmingham, Alabama, and Wichita, Kansas plants of Vulcan Materials, Inc., did not corroborate this contention. Neither plant was reportedly involved in the distribution of any explosives, but explosives containing 2-nitropropane for rock quarrying may be used by the Wichita facility.§

A review of available literature did not yield significant information on use of 2-nitropropane in the explosives industry. Data on its presence in air, water, or land emissions were not found. Detailed studies of the manufacturing processes, chemical formulation, production centers, and the consumption of explosives did not address the use of 2-nitropropane (USEPA 1975, 1976, 1977c).

^{*}M. Irving, DuPont de Nemours, Inc.: personal communication with T. Shannon, JRB Associates, January 1980.

[†] Dr. Chang, Bureau of Explosives: personal communication with T. Shannon, JRB Associates, 1980.

[§] R. McKee, Vulcan: personal communication with T. Shannon, JRB Associates, January 1980.

Use of 2-nitropropane as a rocket propellant was also explored. A review of available literature did not yield any significant information on its use in this industry. A NASA in-house review, conducted upon request by JRB, did not reveal any awareness of the use of 2-nitropropane as a rocket propellant.* A member of the Aerospace Industrial Association of America, although familiar with use of 2-nitropropane as a rocket propellant, did not believe its use was widespread. He characterized it as a high-energy, unstable chemical propellant. An official of the Chemical Propulsion Information Agency stated that the use of 2-nitropropane as a rocket propellant is very limited. He reported that probably the agency did not possess information that would be useful in quantitative use of 2-nitropropane.§

Attempts to estimate the amounts of use and emissions of 2-nitropropane by the explosives and rocket propellant industry were hindered by substantial data gaps. Although it is likely that 2-nitropropane is used as a blasting agent in the explosives industry, quantitative data to corroborate this fact were unavailable. It is likely that 2-nitropropane is being marketed as a blasting agent in the form of a prill, although it presently has a restricted market. Also, it is probably used as a volatile solvent in the casting-powder process of some double base propellants.

- (3) Dyes. According to IMC, 2-nitropropane can be used to dissolve many types of dyes, such as nigrosine and induline dyes. However, its use in this capacity could not be documented in our literature search or industry contacts. According to an official of Atlantic Chemical, 2-nitropropane is not widely used in the dye business because this chemical is under consideration for classification as a carcinogen. A representative of American Cyanamid, a U.S. producer of nigrosine and induline dyes, reported that 2-nitropropane is not used in the manufacture of either dye or during their application by the user. This is because the chemical is expensive and "may be" a carcinogen.** We conclude that there is no evidence of 2-nitropropane usage in dye manufacturing and application.
- (4) Gasoline additives. When nitroparaffins, including 2-nitropropane, are substituted for hydrocarbon fuels, power output of Otto cycle (gasoline) engines is increased 6 percent because more fuel is burned per unit of air. Smoke generation is reduced 50 percent. Various nitroparaffins, including 2-nitropropane, have also been used as fuel additives in model engines and racing cars for short distances (Kirk-Othmer 1964).

^{*}F. Stephenson, NASA: personal communication with T. Shannon, JRB Associates, January 1980.

TM. Snodgrass, AIAA: personal communication with T. Shannon, JRB Associates, January 1980.

[§]R. Brown, CPIA: personal communication with T. Shannon, JRB Associates,

January 1980.

TB. Bochnar, Atlantic Chemical Corp.: personal communication with P. Le., JRB Associates, January 1980.

^{**}S. Greber, American Cyanamid: personal communication with P. Le, JRB Associates, January 1980.

However, investigations by JRB did not reveal any use of 2-nitropropane as a fuel additive. A laboratory official at Gulf Oil, Philadelphia, had not encountered the use of 2-nitropropane as either a commercial gasoline and diesel fuel additive or as a racing car fuel additive.* The director of the racing fuel formulation laboratory of Sun Oil's Marcus Hook refinery also reported that 2-nitropropane is not used as an additive in either their commercial gasoline or diesel fuels or racing fuel formulations.† A representative of the American Petroleum Institute also could not confirm the use of 2-nitropropane as a fuel additive.§ We conclude that there are no significant emissions of 2-nitropropane as a result of its use as a fuel additive.

(5) Other uses. Other possible nonconsumptive uses of 2-nitropropane include pesticides, rubber, model cars, smoke reducers, and as a solvent and stabilizer.

Chloropicrin, and old industrial chemical and military gas, is used extensively today as an insecticide, fungicide, soil sterilizer, and fumigant. One relatively outdated source (Kirk-Othmer 1964) reported that the pesticide is composed of a mixture which includes 2-nitropropane. However, review of USEPA/OPTS 1979 Pesticide Product Information files indicates that none of the 195 products containing chloropicrin as an active ingredient include 2-nitropropane in their formulation (USEPA 1979a). Rather, it is possible that chloropicrin (or trichloronitromethane) contains 2-nitropropane residual impurities, since the base chemical, nitromethane, is produced in the same process that yields 2-nitropropane and other nitroparaffins. However, residual 2-nitropropane would comprise much less than 0.1 percent of pesticide formulations containing chloropicrin, because nitromethane itself contains no more than 0.1 percent nitropropane. We therefore believe that pesticide formulation and usage represent an insignificant source of 2-nitropropane releases.

The rubber industry has a wide range of processes requiring solvents which could possibly include 2-nitropropane. However, no information was found on the use of 2-nitropropane in any rubber formulation processes. 2-Nitropropane has also been identified as being used in model car fuels and as a solvent and stabilizer for a wide range of chemical reactions. As with rubber, significant information detailing the use of 2-nitropropane in such applications was unavailable. Based on the chemical and physical properties of 2-nitropropane, JRB believes that it may be used as a solvent in the above areas.

(6) Releases from miscellaneous uses. The total amount of 2-nitropropane used in all the miscellaneous applications discussed above can be estimated by determining all 2-nitropropane unaccounted for based on the

^{*}Mr. Bower, Gulf Oil: personal communication with T. Shannon, JRB Associates, January 1980.

[†]B. Burtder, Sun Oil: personal communication with T. Shannon, JRB Associates, January 1980.

[§]M. Tiffany, API: personal communication with T. Shannon, JRB Associates, January 1980.

1977 production total of 14,000 kkg. After summing total quantities exported (1,400 kkg), consumptively used (7,000 kkg), used in printing inks (2,900 kkg) and surface coating formulations (1,600 kkg), there are 1,100 kkg of the compound still unaccounted for. We assume that this total is divided among uses in adhesives, explosives, propellants, dyes, and other miscellaneous applications.

Because 2-nitropropane is assumed to be used principally as a solvent in the miscellaneous applications discussed above, the distribution of environmental emissions was assumed to be similar to that from the surface coatings industry, where 2-nitropropane is also used primarily as a solvent. Of 2-nitropropane used by the surface coatings industry, I percent is destroyed, 99 percent is emitted to air, and a negligible amount is released to waste water; there were no land emissions.

Applying these percentages to the 1,100 kkg of 2-nitropropane used by various miscellaneous uses, the emissions are as follows:

Destruction:

11 kkg

Air:

1,089 kkg

Water:

neg

Land:

0 kkg

3.2.4 Exports

In 1979, approximately 10 percent of the total production of 2-nitropropane (or 1,400 kkg) were exported. Most of the exports were to the IMC plant in West Germany.* Releases of 2-nitropropane during transportation, storage, and handling during export are considered to be negligible.

^{*}G. Hess, IMC: personal communication with P. Le, JRB Associates, January 1980.

4.0 RELEASE OF 2-NITROPROPANE FROM NITROMETHANE, NITROETHANE, AND 1-NITROPROPANE USES

The amount of 2-nitropropane present in nitromethane products is less than 0.1 percent by weight (Riddick and Bunger 1970). From this percentage and the amount of nitromethane produced (8,750 kkg), the total quantity of 2-nitropropane is estimated as less than 8.8 kkg.

Nitromethane is used as a rocket fuel, and as a solvent in the surface-coating industry (Merck 1976). By assuming that use as a solvent is the predominant use, we conclude that all 2-nitropropane (8.8 kkg) present as contaminant in nitromethane in 1979 was released to the environment.

Nitroethane production in 1979 was estimated at 1,400 kkg. The level of 2-nitropropane contamination of nitroethane is reported at 3 to 4 percent (Riddick and Bunger 1970). Thus the quantity of 2-nitropropane contained in nitroethane in 1979 was estimated at 42 to 56 kkg, with an average of 50 kkg.

According to the Merck Index (1976), nitroethane is mainly used as a solvent in the synthesis of organic chemicals. It is also used experimentally as a liquid propellant. Because nitroethane is used principally as a solvent, we assume that all of the 2-nitropropane contained in nitroethane is released to the environment through volatilization.

The level of 2-nitropropane contamination in 1-nitropropane is estimated at 3 to 4 percent by weight (3.5 percent) (Riddick and Bunger 1970). The production of 1-nitropropane in 1979 was estimated at 8,750 kkg. Therefore, 1-nitropropane manufactured in 1979 was calculated to contain 305 kkg of 2-nitropropane.

The uses of 1-nitropropane are the same as those for 2-nitropropane (Merck 1976). The information on the quantity of consumptive and nonconsumptive uses of 1-nitropropane does not exist in the literature. Therefore, to quantify the amount of 2-nitropropane in each type of 1-nitropropane use, we assume that the usage percentages are the same as those presented in Chapter 3 for nonconsumptive and consumptive uses of 2-nitropropane: 40 percent and 60 percent, respectively. By using these percentages, we therefore can estimate the amount of 2-nitropropane present in consumptive and nonconsumptive uses of 1-nitropropane at 185 kkg and 120 kkg, respectively.

l-Nitropropane can be used captively in the production of hydroxyl-ammonium sulfate and other derivatives. Hydroxylamine salts can be prepared by the hydrolysis of l-nitropropane with acid and water. The reaction of l-nitropropane with H₂SO₄ and water produces hydroxylammonium acid sulfate. This reaction can be accomplished in a glass-lined, agitated reactor. The product of this reaction is then reacted with an aqueous 85 percent methanol solution in another glass-lined reactor to produce crystalline hydroxylammonium sulfate. Propionic acid is a by-product

(Reidel 1956). Figure 4.1 presents a flow diagram of the production of hydroxylammonium sulfate.

During the production of 1-nitropropane derivatives, we can assume that most of the 2-nitropropane contaminant is destroyed or reacted with other chemicals. Thus, the final 1-nitropropane derivative products would probably contain a minimal amount of 2-nitropropane. Assuming that 99.9 percent of the 2-nitropropane contaminant is destroyed or chemically changed during the production and processing of these derivatives, then the amount of 2-nitropropane remaining in the final products is 0.20 kkg.

The nonconsumptive uses of 1-nitropropane are reported to be the same as those for 2-nitropropane (Merck 1976). Thus, we can assume that the fate of the 2-nitropropane contaminant going to these nonconsumptive uses is as follows: 99 percent is released to the air, and 1 percent is destroyed. Using these percentages, we estimated that in 1979, of the total amount of the 2-nitropropane contaminant in 1-nitropropane used nonconsumptively (120 kkg), 119 kkg were released to the air and 1 kkg was destroyed. (These values are only estimates and should be verified in further studies.)

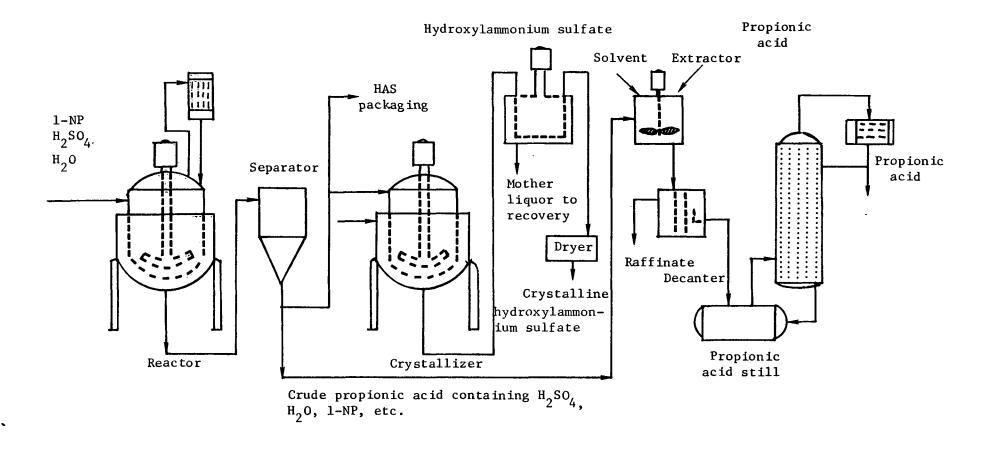


Figure 4.1 Flow Diagram of Manufacture of Hydroxylammonium Sulfate

5.0 RELEASE SOURCE EVALUATION

The total environmental releases of 2-nitropropane in 1979 are estimated to be 5,715 kkg. Table 5.1 summarizes the releases by the source of emission, quantity released, and destination (air or water); these quantities have been determined previously in the report. Table 5.2 categorizes these emissions by usage and geographic location.

The majority of 2-nitropropane emissions (78 percent or 4,450 kkg) come from the use of 2-nitropropane as a solvent in printing inks and surface coatings. The remaining 22 percent of the releases (1,265 kkg) result from the direct production of 2-nitropropane, miscellaneous uses of 2-nitropropane, and uses of other nitroparaffin products.

Most 2-nitropropane releases (5,714 kkg) are to the atmosphere. Water releases are negligible compared to the total releases. There are no land releases. The largest source of air releases is in the use of 2-nitropropane as a solvent in printing inks.

Table 5.1 Summary of Environmental Releases of 2-Nitropropane, 1979

Sources of releases	Total releases (kkg)		r releases (% of total)	Land releases (% of total)		er releases (% of total)
Direct production	20	19	0.3		1	100
Uses	5,543	5,543	96.6		0	0
Contaminants of other nitro-paraffin products	178	178	3.1		0	0
Totals	5,741	5,740	100		1	100

Table 5.2 Categorization of 2-Nitropropane Environmental Releases

		Total e	nvironment	al releases
2	Geographic	Air	Water	Land
Source	location	(kkg)	(kkg)	(kkg)
Direct				
production	l plant in LA	19	1.0	
Consumptive				
uses	l plant in LA	Neg	Neg	
Printing				
inks	All over U.S.	2,870	Neg	
Surface		-		
coatings	All over U.S.	1,584	Neg	
Miscellaneous				
uses		1,089	Neg	
Contaminants				
of NM, NE,				
1 -NP	All over U.S.	178	Neg	

6.0 SUMMARY OF DISPOSAL AND DESTRUCTION OF WASTES

This chapter summarizes the amount of 2-nitropropane released to the environment during the destruction and disposal of wastes containing 2-nitropropane; these releases have been discussed previously in the report. Table 6.1 summarizes the amount of waste, type of waste, and area of release.

2-Nitropropane wastes are produced during the nitration of propane, formulation and use of surface coatings, and the formulation of printing inks. The total amount of 2-nitropropane in solid and liquid waste is estimated to be 231 kkg.

Incineration and biodegradation destroy 92 percent (212 kkg) of this waste, the remaining quantity (18 kkg) is either released to air or water.

Table 6.1 Releases from Disposal/Destruction of 2-Nitropropane-Containing Wastes (liquid and solid wastes)

Process	Waste (kkg)	Destroyed by incineration/ waste treatment (kkg)	Released to air after control (kkg)	Released to water after control (kkg)
Vitration of				
propane	186	167	18	1
Formulation of printing inks	29	29	neg	neg
ormulation of surface				
coatings	16	16	neg	neg
Total	231	212	18	1

7.0 DATA GAPS AND RECOMMENDATIONS

Numerous data gaps were encountered during the preparation of this report. These data gaps were due to incomplete literature on pertinent subjects, the confidentiality of much industrial information, the lack of research in various areas, and the lack of monitoring data within the industrial facilities.

The most important area for which data were lacking was the process descriptions and associated emission factors for 2-nitropropane manufacture as well as for its primary and secondary uses. The emissions can be better estimated when data are available on the emission factors for each process, waste treatment methods used by the manufacturers, and the quantity of 2-nitropropane present in the product.

With regard to the uses of 2-nitropropane, there were serious information gaps, both qualitative and quantitative, on primary and secondary products. Basic information was unavailable for the major primary uses (such as quantity of 2-nitropropane used, manufacturers, and locations). For the minor primary uses, data on the amount of 2-nitropropane used were lacking. Other data gaps included percentage breakdowns for each primary use, the rate of degradation of 2-nitropropane-containing products, site of manufacture, and site of use of manufactured products.

The materials balance for 2-nitropropane contains data gaps that could be resolved primarily with monitoring, sampling, and additional information detailing the amounts of 2-nitropropane used by various industries. Table 7.1 lists the major data gaps for 2-nitropropane and recommendations of methods for their solution.

Table 7.1 Data Gaps and Recommendations

Data Gaps	Recommendations
A. Production	
 Description of current processes and associated emissions 	Chemical engineering literature; contact IMC; Manufacturing Chemists Association
Quantity of each form of nitroparaffins produced	Contact IMC; Manufacturing Chemists Association; extensive literature search
 Amount of 2-nitropropane present as impurity in each form 	Contact IMC; extensive literature search; Manu- facturing Chemists Association; laboratory analyses
4. Waste Incineration	
 a. Whether 2-nitropropane is inadvertently produced during incineration 	Literature search; contact with municipal incin- eration plants
b. Type of emission control system and associated releases	Contact with incineration plants; contact IMC
B. Exports	
1. Quantity exported	Bureau of Census; export agents; contact with

Table 7.1 Data Gaps and Recommendations (continued)

Data	Gaps	Recommendations		
	ge, handling, transpor- n releases	Department of Transportation; port authorities; contact with manufacturers		
3. Ports	of exit	Contact with manufacturers; Bureau of Census; export agents		
C. Uses				
l. Consu	mptive uses			
a. 2-	Nitro-2-methyl-l-propanol			
1.	Production capacity	Contact manufacturer		
2.	Current process descrip- tion and associated releases	Contact manufacturer; chemical engineering literature; monitoring		
3.	Amount of 2-nitropro- pane used	Contact manufacturer; extensive literature search; Manufacturing Chemists Association; laboratory analysis		
4.	Secondary products - production processes and associated 2-nitro- propane releases	Contact manufacturer; extensive literature search		
b. Am	inohydroxy compounds			
1.	Production capacity	Contact manufacturer		

Table 7.1 Data Gaps and Recommendations (continued)

Da	ta Gaps	Recommendations	
2.	Process description and associated releases	Chemical engineering literature; contact manufacturer; monitoring	
3.	Impurity level of 2- nitropropane	Contact manufacturer; extensive literature search; Manufacturing Chemists Association; laboratory analysis	
4.	Secondary products - production processes and associated releases	Contact manufacturer; extensive literature search	
	nsumptive Uses		
a. Su	rface coatings		
	Cellulose coatings		
1.			
1.	a. Quantity of 2-nitropro- pane used	Contact IMC; contact cellulose coatings manufacturers	
1.		•	

Table 7.1 Data Gaps and Recommendations (continued)

Data Ga	ıps	Recommendations
d.	Description of production process and associated emissions	Chemical engineering literature; contact manufacturers; monitoring
е.	Manufacturers, locations, and plant capacities	Contact IMC; Chemical Economics Handbook; Manufacturing Chemists Association; contact manufacturers
2. Vinyl c	oatings	
a.	Capacity of producers	Contact manufacturers
b.	Description of production process and associated emissions	Chemical engineering literature; contact manufacturers; monitoring
c.	Amount of 2-nitropropane used	Extensive literature search; contact with manu- facturers; laboratory analysis
d.	Process descriptions and associated emissions for secondary products and uses	Extensive literature search; contact with manu- facturers; Manufacturing Chemists Association
e.	Manufacturers, locations, and plant capacities	Contact IMC; Chemical Economics Handbook; Manufacturing Chemists Association; contact manufacturers

Table 7.1 Data Gaps and Recommendations (continued)

	Data	Gaps	Recommendations
3.	Ерох	y Coatings	
	a.	Capacity of producers	Contact manufacturers
		Description of production processes and associated emissions	Chemical engineering literature; contact manu- facturers; monitoring
		Identification of pro- ducts	Manufacturing Chemists Association; contact IMC; contact coating manufacturers
	•	Manufacturers and loca- tions	Contact IMC
		Description of production process and associated emissions	Chemical engineering literature; contact manu- facturers; monitoring
4.	Othe	r Miscellaneous Coatings	
	a.	Capacity of producers	Contact manufacturers
		Description of production process and associated emissions	Chemical engineering literature; contact manufacturers; monitoring
		Amount of 2-nitropropane used	Extensive literature search; contact with manu- facturers; laboratory analysis

Table 7.1 Data Gaps and Recommendations (continued)

	Data Gaps	Recommendations
	d. Process descriptions and associated emissions for secondary products and uses	Extensive literature search; contact with manu- facturers; Manufacturing Chemists Association
	e. Manufacturers, locations of plants and capacities	Contact IMC; Chemical Economics Handbook; Manu- facturing Chemists Association; contact manu- facturers
b. Pri	nting Inks	
1.	Capacity of producers	Contact manufacturers
2.	Description of production processes and associated emissions	Chemical engineering literature; contact manufacturers; monitoring
3.	Amount of 2-nitropropane used	Extensive literature search; contact with manu-facturers; laboratory analysis
4.	Process descriptions and associated emissions for secondary products and uses	Extensive literature search; contact with manu- facturers; Manufacturing Chemists Association
5.	Manufacturers, location of plants, capacities	Contact IMC; Chemical Economics Handbook; Manufacturing Chemists Association; contact manufacturers; USEPA Effluent Guidelines Divison.

Table 7.1 Data Gaps and Recommendations (continued)

	Data Gaps	Recommendations
c. Adh	nesives	
1.	Amount of 2-nitropropane used	Contact manufacturers; contact IMC
2.	Description of process and emissions of 2-nitropropane	Chemical engineering literature; contact manu- facturers; monitoring
3.	Destruction of wastes	Contact manufacturers
4.	Amount of 2-nitropropane retained as impurity	Chemistry literature; contact manufacturers
5.	Percentage breakdown of uses	Extensive literature search; Chemical Economics Handbook; contact manufacturers; Manufacturing Chemists Association
6.	Process descriptions for uses and associated emission factors	Chemical engineering literature; contact manu- facturers and users
7.	Breakdown products	Chemistry literature; contact manufacturers
8.	End products of each use	Extensive literature search; contact users; Consumer Product Safety Commission
9.	Manufacturers, location of plants, capacities	Contact IMC; Chemical Economics Handbook; Manu- facturing Chemists Association; contact manu- facturers

Table 7.1 Data Gaps and Recommendations (continued)

	Data Gaps	Recommendations
d. Exp	olosives	
1.	Amount of 2-nitropropane used	Contact manufacturers; contact IMC
2.	Quantity produced	Chemical Economics Handbook; contact IMC; USITC
3.	Description of production process and emissions of 2-nitropropane	Chemical engineering literature; contact manufacturers; monitoring
4.	Destruction of wastes	Contact manufacturers
5.	Amount of 2-nitropropane retained as an impurity	Chemistry literature; contact manufacturers
6.	Percentage breakdown of uses	Literature search; Chemical Economics Handbook; contact manufacturers; Manufacturing Chemists Association
7.	Manufacturers, location of plants, capacities	Contact IMC; Chemical Economics Handbook; Manu- facturing Chemists Association; contact manu- facturers
e. Dye	28	
1.	Amount of 2-nitropropane used	Contact manufacturers; contact IMC

Table 7.1 Data Gaps and Recommendations (continued)

		Data Gaps	Recommendations
	5.	Amount of 2-nitropropane retained as an impurity	Chemistry literature; contact manufacturers
	6.	Percentage breakdown of uses	Literature search; Chemical Economics Handbook; contact manufacturers; Manufacturing Chemists Association
	7.	Manufacturers, location of plants, capacities	Contact IMC; Chemical Economics Handbook; Manufacturing Chemists Association; contact manufacturers
g.	nit	taminants in nitroethane (NE), romethane (NM), and l-nitro- pane (1-NP)	
	1.	Percentage breakdown of uses of NE, NM, and 1-NP	Literature search; Chemical Economics Handbook; contact manufacturers; Manufacturing Chemists Association
	2.	Locations of consumers of NE, NM, and 1-NP	Literature search; Chemical Economics Handbook; contact manufacturers; Manufacturing Chemists Association
	3.	Releases of 2-nitropropane associated with production and use of NE, NM, and 1-NP	Contact IMC; contact manufacturers

Table 7.1 Data Gaps and Recommendations (continued)

		Data Gaps	Recommendations
	2.	Quantity produced	Chemical Economics Handbook; contact IMC; USITC
	3.	Description of production process and emissions of 2-nitropropane	Chemical engineering literature; contact manufacturers; monitoring
	4.	Destruction of wastes	Contact manufacturers
	5.	Amount of 2-nitropropane retained as an impurity	Chemistry literature; contact manufacturers
	6.	Percentage breakdown of uses	Literature search; Chemical Economics Handbook; contact manufacturers; Manufacturing Chemists Association
f.	Oth	er Miscellaneous Uses	
	1.	Amount of 2-nitropropane used	Contact manufacturers; contact IMC
	2.	Quantity produced	Chemical Economics Handbook; contact IMC; USITC
	3.	Description of production process and emissions of 2-nitropropane	Chemical engineering literature; contact with manufacturers; monitoring
	4.	Destruction of wastes	Contact manufacturers

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APPENDIX A PROPERTIES OF 2-NITROPROPANE

Table A.1 Properties of 2-Nitropropane

Synonyms	Dimethylnitromethane Isonitropropane
Molecular Formula	CH ₃ CH(NO ₂)CH ₃
Molecular Weight	89.09
Physical State	Colorless liquid
Vapor Pressure	20 mm Hg at 25°C
Boiling Point	120°C
Melting Point	-93°c
Water Solubility	Slightly soluble

Source: USEPA, 1977a

A-1 RELEASE OF 2-NITROPROPANE TO AIR FROM PRODUCT STORAGE TANKS

There are two kinds of releases from storage tanks: loss due to tank breathing, and working loss or loss due to tank cleaning and filling.

According to the AP-42 report (USEPA 1977b), emission factors of 2-nitropropane from "old" fixed roof tanks can be calculated. The following sections discuss in detail methods of estimating the emission of 2-nitropropane from product storage tanks.

(a) Emission of 2-Nitropropane to Air Because of Tank Breathing

Tank breathing losses are defined by the AP-42 report as losses resulting from a tank because of the thermal expansion of existing vapors, vapor expansions as a result of barometric pressure changes, and/or an increase in the amount of vapor because of added vaporization in the absence of a liquid-level change (USEPA 1977b).

The emission factor for 2-nitropropane from a storage tank due to tank breathing can be calculated by means of an equation obtained from the AP-42 report (US EPA, 1977b).

$$L_{B} = (2.21 \times 10^{-4}) \,\mathrm{M} \left[\frac{\mathrm{P}}{14.7 - \mathrm{P}} \right]^{0.68} \quad \mathrm{D}^{1.73} \mathrm{H}^{0.51} (\Delta \mathrm{T})^{0.5} \,\mathrm{F}_{\mathrm{p}} \mathrm{CK}_{\mathrm{C}} \tag{1}$$

where:

 L_p = Fixed roof breathing loss (lb/day)

M = Molecular weight of vapor in storage tank (1b/1b-mole)

P = True vapor pressure at bulk liquid conditions (psia)

D = Tank diameter (ft)

H = Average vapor space height, including roof volume correction (ft)

 ΔT = Average ambient temperature change from day to night (${}^{O}F$)

F = Paint factor (dimensionless)

C = Adjustment factor for small diameter tanks (dimensionless)

 K_C = Crude oil factor (dimensionless)

To calculate the amount of 2-nitropropane lost to the air because of tank breathing, we make the following assumptions:

- 2-Nitropropane is stored in fixed roof tanks, and the tank is in "worn" condition
- All 2-nitropropane is stored for at least one day before it is distributed for other uses
- There are 300 working days in a year
- The ambient temperature is 20° C (68°F)
- The tank volume is 15,000 gallons, the average tank height is 10 feet, the diameter is 16 feet, and the site has 2 tanks
- The tank is painted either white or aluminum
- The liquid level inside the tank is half the average height of the tank
- Ambient temperature change from day to night is 15°F.

Based on the above assumptions, the variables presented in equation (1) can be evaluated as follows:

M = 89 lb/lb mole

D = 16 ft

H = 5 ft

 $\Lambda T = 15^{\circ} F$

 $F_p = 1.14 \text{ (USEPA 1977b)}$

C = 1

 $K_{C} = 1$

The value of the vapor pressure for bulk liquid conditions (20° C) can be calculated by means of the Antoine's equation as follows:

$$Log_{10} P = \frac{-0.2185A}{K} + B$$
 (2)

where:

P = pressure (mm Hg)

K = temperature (degrees Kelvin)

A = 9,476.9 for 2-nitropropane (Weast 1973)

B = 8.164069 for 2-nitropropane (Weast 1973)

By applying these obtained variables to equation (2), the true vapor pressure of 2-nitropropane at 20° C (or 293.15° K) can be estimated as follows: $\frac{(-0.2185)(9,476.9)}{(293.15)} + (8.164069) = 12.6 \text{ mm Hg or } 0.24 \text{ psia}$

The emission factor of 2-nitropropane associated with tank breathing loss can then be calculated by inserting the determined values for variables in equation (1). The emission factor is estimated as follows:

$$L_B = (2.21 \times 10^{-4}) (89) \left(\frac{0.24}{14.7-0.24}\right) 0.68 \frac{1.73}{(16)} \frac{0.51}{(5)} \frac{0.5}{(15)} \frac{0.5}{(1.14)(1)(1)} = 1.47 \text{ lb/day or } 6.1 \times 10^{-4} \text{kkg/day/tank}$$

Assuming that there are 300 working days in a year, the annual <u>uncontrolled</u> emissions from product storage due to tank breathing are:

We assume that the emission of 2-nitropropane due to tank breathing can be controlled by a refrigerated system that can achieve an 80 percent control efficiency. The typical efficiency range of such recovery system is from 65 to 95 percent. Therefore the estimated release rate is 20 percent. The controlled emissions can be calculated as follows:

Uncontrolled Emission of 2-Nitropropane (0.2) =
$$\begin{pmatrix} \text{Controlled Emission} \\ \text{Control Device} \end{pmatrix}$$
 = $\begin{pmatrix} \text{Controlled Emission} \\ \text{Control Device} \end{pmatrix}$ = $\begin{pmatrix} \text{Controlled Emission} \\ \text{Control Device} \end{pmatrix}$ = $\begin{pmatrix} \text{Controlled Emission} \\ \text{Control Device} \end{pmatrix}$ = $\begin{pmatrix} \text{Controlled Emission} \\ \text{Controlled Emission} \\ \text{Controlled Emission} \end{pmatrix}$ = $\begin{pmatrix} \text{Controlled Emission} \\ \text{Controlled Emission} \\ \text{Controlled Emission} \\ \text{Controlled Emission} \end{pmatrix}$

(b) Emission of 2-Nitropropane to Air During Tank Handling and Tank Cleaning

Environmental loss to air due to tank handling and tank cleaning is defined as working loss. Using the equation given by the AP-42 report, the emission factor for working loss can be estimated (USEPA 1977b). The equation is as follows:

$$L_W = (2.4 \times 10^{-2}) \text{ MPK}_N K_C$$
 (3)

where:

 L_W = Fixed roof tank working loss (1b/10³gal)

M = Molecular weight of vapor in storage tank (1b/1b mole)

P = True vapor pressure at bulk liquid conditions (psia)

K_M = Turnover factor

 K_C = Crude oil factor

The following assumptions are made to determine the value of each variable stated above:

- The density of 2-nitropropane at 20°C is 0.9876 kg/l (Weast 1973)
- The vapor pressure of 2-nitropropane at 20°C is estimated at 0.24 psia (see (a) above)
- The storage tank capacity is 15,000 gal (see (a) above)
- The crude oil factor is 1 (USEPA 1977b)
- The production site has 2 storage tanks (15,000 gal)

Based on the above assumptions, the turnover factor K_N is estimated at 0.41 (USEPA 1977b). The emission factor for working loss can also be calculated by using the above factors in equation (3).

$$L_W^{=}$$
 (2.4 x 10⁻²)(89)(0.24)(0.41) (1) = 2.1 x 10⁻¹ 1b/10³gal or 9.5 x 10⁻⁵ kkg/10³ gal (+10%)

The annual throughput volume of 2-nitropropane is calculated as follows:

(Production of 2-Nitropropane) (Density of 2-Nitropropane) = Annual Throughput Volume (14,000 kkg)/(0.9876 kkg/
$$10^3$$
 l)⁻¹ = 14 x 10^6 l or 3.7 x 10^6 gal

The quantity of 2-nitropropane lost in <u>uncontrolled</u> emissions to the air because of working loss can then be estimated as follows:

Annual Throughput
$$(2)$$
 Tanks $(3.7 \times 10^6 \text{gal}) (9.5 \times 10^{-5} \text{ kkg/}10^3 \text{ gal/tank}) = 7.0 \times 10^{-1} \text{ kkg}$

Uncontrolled Emission of 2-Nitropropane Due to Working Loss

Assuming that the working losses of 2-nitropropane from product storage can be controlled by a vapor recovery system with 20 percent release rate (Typical range of efficiency of the vapor recovery system is from 65 to 95 percent), then the controlled emissions can be calculated as follows:

Uncontrolled Emission Due to Working Loss (0.2)

[Inefficiency Factor of Control Device] = Controlled Emissions

[Inefficiency Factor of Control Device] = 1.4 x
$$10^{-1}$$
 kkg

A-2 RELEASE OF 2-NITROPROPANE DURING LOADING AND TRANSPORTATION

Loading losses from tank car and tank truck operations are major sources of emission. Loading losses occur as vapors residing in empty cargo tanks are displaced to the atmosphere by the liquid being added into the tank (USEPA 1977b).

The emission factor for loading tank cars and trucks is given as follows (USEPA 1977b):

$$L_{L} = 12.46 \frac{SPM}{T}$$

where: $L_{T} = Loading loss (1b/10³ gal of liquid loaded)$

M = Molecular weight of vapors (1b/lb mole)

T = Bulk temperature of liquid loaded (°R)

P = True vapor pressure of the liquid loading (psia)

S = Saturation factor.

To calculate the emission factor for loading operations, the following conditions and properties are used:

- 1. The only quantity that is shipped is the amount used for nonconsumptive uses and export (7,000 kkg)
- 2. The density of 2-nitropropane is 0.988 g/ml
- The bulk temperature of the liquid loading is 25°C (or 77°F or 537°R)
- 4. From USEPA 1977b, the S factor is 0.6, assuming that the operation is accomplished through submerged loading with normal dedicated service.
- 5. The vapor pressure of 2-nitropropane at 25°C is 0.32 psia
- 6. The molecular weight of 2-nitropropane is 89 lb/lb-mole

Using this factor, the loading loss can be calculated as follows:

$$L_{L} = \frac{12.46 (0.6)(0.32)(89)}{537} = 0.4 \text{ lb/lo}^3 \text{ gal}$$

The total amount of 2-nitropropane shipped is 7,000 kkg $(7.1 \times 10^{-6} \text{ L})$ or 1.9 x 10^{6} gal). Therefore, the total quantity of 2-nitropropane lost during loading is $(0.4 \text{ lb/}10^{3} \text{ gal})(1.9 \times 10^{6} \text{ gal}) = 760 \text{ lb}$ or 0.3 kkg. Assuming that the unloading loss is equal to the loading loss, the amount of 2-nitropropane released during unloading in the United Stated is:

$$(0.4 \text{ lb/l0}^3 \text{ gal})(5,600 \text{ kkg}) = \frac{10^3 \text{ l}}{.988 \text{ kkg}} = \frac{\text{l/gal}}{3.785 \text{l}} = 600 \text{ lb or } 0.3 \text{ kkg}$$

During the transportation of volatile liquids, small quantities of vapor are expelled from the tank due to temperature and barometric changes. The loss during transportation can be estimated using the following equation (USEPA 1977b):

$$L_{\mathbf{r}} = 0.1PW$$

where:

L_T = Transit loss (lb/week-10³gal transported)

P = True vapor pressure of the transported liquid (psia)

W = Density of the condensed vapors (1b/gal)

If the density of the condensed vapor of 2-nitropropane is equal to the liquid density (as is true for most pure compounds), then W is equal to 0.988 g/ml or 8.18 lb/gal. The true vapor pressure was given previously as 0.32 psia. Therefore the transit loss can be estimated as follows:

$$L_{T} = (0.1)(0.32)(8.18) = 0.26 \text{ lb/}10^{3}\text{gal-week.}$$

If we assume that the total amount of liquid transported is 1.5×10^6 gal (see calculations in the previous section) and residence time of the transported material is 1 week, then

$$L_T = \left(\frac{0.26 \text{ lb}}{10^3 \text{gal-week}}\right) (1 \text{ week}) (1.5 \times 10^6 \text{gal}) = 390 \text{ lb or } 0.18 \text{ kkg}$$

Therefore the total amount of 2-nitropropane released to the air during all phases of loading and transportation is 0.18 kkg + 0.6 kkg = 0.8 kkg.

						
TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)						
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1						

Project Officer - Michael Callahan

16. ABSTRACT

A Level I materials balance was performed for 2-nitropropane for the year 1979. Releases to the respective environmental media were estimated for the processes in which 2-nitropropane is produced, consumed, used nonconsumptively, destroyed, or carried over into products. Of the estimated 1979 production of 14,000 kkg, 5,715 kkg (41 percent) were estimated to have been released to the environment. The major contributor to this release estimate was evaporation of 2-nitropropane used as a solvent in printing ink and surface coatings (4,450 kkg; 78 percent of releases). Atmospheric emissions accounted for essentially all 2-nitropropane released. The report describes the estimation methods used, and characterizes the reliabilities of the estimated values. Data gaps are discussed and suggestions are made for obtaining the information required.

17.	KEY WORDS AND DOCUMENT ANALYSIS						
a.	DESCRIPTORS	b.IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group				
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		{					
8. DISTRIBU	TION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES				
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		Unclassified					