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DYNAMAC
CORPORATION

NALED

Product Chemistry

Task 2: Topical Discussions

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Final Report

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Arlington, Virginia 22202

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PRODUCT CHEMISTRY

Task 2

Table of Contents

	<u>Page</u>
INTRODUCTION	1
CHEMICAL IDENTITY	2
MANUFACTURING PROCESS	2
FORMATION OF UNINTENTIONAL INGREDIENTS	3
PERCENT OF ACTIVE INGREDIENTS IN PESTICIDE PRODUCTS	3
PRODUCT ANALYTICAL METHODS AND DATA	4
PHYSICAL/CHEMICAL PROPERTIES	4
REFERENCES	6

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PRODUCT CHEMISTRY

Task 2

Introduction

FIFRA 3(c)(2)(A) required the Agency to establish guidelines for registering pesticides in the United States. The Agency requires registrants to provide quantitative data on all added ingredients, active and inert, which are equal to or greater than 0.1% of the product by weight.

To establish the composition of products proposed for registration, the Agency requires data and information not only on the manufacturing and formulation processes, but also a discussion on the formation of manufacturing impurities and other product ingredients, intentional and unintentional. Further, to assure that the composition of the product as marketed will not vary from the composition evaluated at the time of registration, applicants are required to submit a statement certifying upper and lower composition limits for the added ingredients, and upper limits only for some unintentional ingredients. Guidelines Subpart D (43 FR 29696) suggests specific precision limits for ingredients based on the percentage of ingredient and the standard deviation of the analytical method.

In addition to the data on product composition, the Agency also requires data to establish the physical and chemical properties of both the pesticide active ingredient and its formulations. For example, data are needed concerning the identity and physical state of the active ingredient (e.g., melting and boiling point data, ambient vapor pressure and solubility).

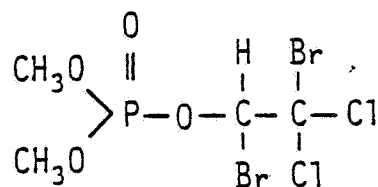
Corresponding to each of the Topical Discussions listed below is the number of the Section in the "Proposed Guidelines for Registering Pesticides" of July 10, 1978 (43 FR, No. 132, 29696), which explains the minimum data the Agency will need to adequately assess the product chemistry of naled.

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Chemical Identity.....	163.61-3
Manufacturing Process.....	163.61-4
Formation of Unintentional Ingredients.....	163.61-5
Active Ingredient Limits in Pesticide Products.....	163.61-6
Product Analytical Methods and Data.....	163.61-7
Physical/Chemical Properties.....	163.61-8

1. Chemical Identity

In the United States, naled is the ANSI-approved common name for a halogenated organophosphorus insecticide marketed by Chevron Chemical Co.



The chemical name for naled is 1,2-dibromo-2,2-dichloroethyl dimethyl phosphate. Other names include Dibrom®, Ortho-Dibrom®, RE 4355, and phosphoric acid 1,2-dibromo-2,2-dichloroethyl dimethyl ester. Other identifying characteristics and codes are:

Empirical Formula: C₄H₇O₄PBr₂Cl₂ (00074653, 00074724, and GS092040).

Molecular Weight: 381 (00074653, 00074724, and GS092040).

CAS Registry No.: 300-76-5.

ENT Registry No.: 24988.

Shaughnessy No.: 034401.

2. Manufacturing Process

In the United States, technical naled is produced by Amvac Chemical Corp. and Shell Chemical Co. for Chevron Chemical Co. In Israel, technical naled is produced by Makhteshim-Agan and in Spain by Ugimica, S.A. No naled is imported into the United States; about [REDACTED] are exported. The U.S. Patent No. for naled is 2,971,882 (Chevron Chemical Co., 1966, 00074653).

COMMERCIAL/FINANCIAL INFORMATION IS NOT INCLUDED

The technical also serves as the manufacturing-use product. Naled formulations (dusts, impregnated materials, and emulsifiable concentrates) are registered by at least 23 companies, including Chevron Chemical Co.

Confidential Appendix A contains a description of the manufacturing process submitted by Chevron Chemical Co. (00074653 and 00074791). Purities of two intermediates were given. It is not known whether Amvac Chemical Corp. and Shell Chemical Co. use the same manufacturing process as that submitted by Chevron Chemical Co.; if not, descriptions of these processes must be submitted to satisfy data requirements. This constitutes a data gap.

3. Formation of Unintentional Ingredients

Three confidential business documents submitted by Chevron Chemical Co. (00065493, 00065494, and GS092040) contain qualitative and quantitative information on the impurities present in technical naled; this information is presented in Confidential Appendix B. Since the methods used were not adequately described, the compounds identified may be considered only as potential impurities. Data gaps thus include the identification and quantification of impurities in technical naled.

4. Percent of Active Ingredients in Pesticide Products

Technical naled contains the active ingredient at [REDACTED] according to two confidential Chevron Chemical Co. documents (19??, 00065493 and 1971, 00065494). The GC method D-IX of Chevron (1966, 00074655) was used to establish the above naled limits although the number of batches tested was unspecified. Using the same method, Chevron Chemical Co. (1966, 00074653) found that 10 samples of technical naled received over a 3-month period from Shell Chemical Co. contained naled at [REDACTED]

QUALITY CONTROL PROCEDURE INFORMATION IS NOT INCLUDED

The absence of data representing five or more production batches and the lack of limit certification constitute data gaps. In addition, updates of the limits and the methods presently used for quality control (including recovery and sensitivity data) are required; the absence of these updates constitutes a data gap.

5. Product Analytical Method and Data

Three Chevron Chemical Co. documents and one published study describe analytical methods for the determination of naled in the technical and in formulated products. A method involving the potentiometric titration of Br^- is inadequate because it is not specific for naled (00074724). The GC methods (00074655, 00074846, and GS092006) also are inadequate because: detection limits and validation data were not provided, data for technical naled or formulated products were not reported, and a confirmatory procedure was not detailed. An update of the method(s) used for quality control of the technical and formulated products of naled is required,

Several methods were reported by Hayman et al. of Chevron Chemical Co. (00065494) to be useful for the determination of impurities in technical naled. The methods were not adequately described and no recovery or sensitivity data were provided. These deficiencies constitute data gaps.

IR spectra were provided for purified naled by Chevron Chemical Co. (00074653). The compound absorbed strongly at ~ 860 , 900, 1020, 1060, 1120, 1280, and 1295 cm^{-1} .

6. Physical/Chemical Properties

Technical naled also serves as the manufacturing-use product.

90% Technical naled/manufacturing-use product manufactured by Amvac Chemical Corp. and Shell Chemical Co. for Chevron Chemical Co.

- | | |
|---|--|
| 1. <u>Color</u> : ^{a,b} | Light, straw-colored (white when pure). |
| 2. <u>Odor</u> : ^{a,b} | Slightly pungent. |
| 3. <u>Melting point</u> : | 25.56°C ^b (27-28.5°C ^{a,c} or 25.5-26.5°C ^d for pure compound). |
| 4. <u>Solubility</u> : ^{a,b,c} | Limited solubility (1-5%) in aliphatic solvents; highly soluble in oxygenated solvents such as ketones and alcohols; low solubility in water (0.2 g/100 ml at 23.3°C ^a). |

5. Stability: Naled in saturated aqueous solution (2 g/l) is rapidly hydrolyzed at 23.3°C^a (naled of unspecified purity in aqueous solution is not hydrolyzed at 0°C and has half-lives of ~13 and ~2 days at 25 and 40°C, respectively^{c,d}; complete hydrolysis occurs under reflux within 4 hours in distilled water or in the presence of excess NaOH^d).
6. Octanol/water partition coefficient: Not reported.
7. Physical state:^{a,b} Oily liquid (pure compound is a low melting point solid).
8. Density or specific gravity: 1.97 at 20°C^b; 1.96^{a,c}; 1.465^a (1.96 for pure compound^d) (temperatures unspecified).
9. Boiling point: 110^b or 120°C^{a,c} at 0.5 mmHg (108-110°C at 0.25 mmHg for pure compound^d).
10. Vapor pressure:^{a,b,c} 2×10^{-4} mmHg at 20°C.
11. pH: Not reported.
12. Storage stability:^c No breakdown of the technical material (source: Shell Chemical Co.) occurred within 18 months at ambient temperatures and 2.5% degradation occurred at 38°C over the same period.
13. Flammability:^a Flash point of 53°C.^e
14. Oxidizing or reducing action:^a Not an oxidizing or reducing agent.
15. Explosiveness:^a Not explosive.
16. Miscibility:^{a,b} Miscible in most organic solvents; emulsifiable in water.
17. Viscosity: 22 cp at 20°C^a or 210-250 sec Saybolt at 37.8°C^b.
18. Corrosion characteristics: Corrosive to steel, aluminum, and magnesium^a; corrosive to all the above as well as copper and brass when in the presence of water^b.

^aFrom 00074790.

^bFrom GS092040.

^cFrom 00074653.

^dFrom 00074724.

^eA flash point of 53°C appears low for a compound having the chemical structure of naled. Confirmation of this figure is thus requested.

The absence of data for any of the physical/chemical properties above constitutes data gaps. Data gaps also exist for "Density or specific gravity" due to conflicting values and for "Flammability" pending the submission of confirmation of the flash point of Naled.

References

Chevron Chemical Company (1965?) Product Chemistry Data for Chevron Naled Technical. (Unpublished study received Oct. 17, 1977 under 239-1633; CDL: 232095-A). (00074790)

Chevron Chemical Company (1966) Name, Chemical Identity and Composition of the Pesticide Chemical: Dibrom. (Unpublished study received Sep. 12, 1966 under 7F0532; CDL:092821-H). (00074653)

Chevron Chemical Company (1966) Ortho Method of Analysis--D-IX-a: Dibrom. Naled by Gas Chromatograph. Method dated May 27, 1966. (Unpublished study received Sep. 12, 1966 under 7F0532; CDL:092521-J). (00074655)

Chevron Chemical Company (1974) Chevron-Naled: Formulator's Manual. (Unpublished study received Oct. 22, 1974 under 239-1633, Accession No. 233083). (GS092040)

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Hayman, E.L.; Friedrich, W.E.; Carlstrom, A.A. (1971) Determination of Impurities in Technical Dibrom. (Unpublished study received Mar. 19, 1976 under 239-2444; submitted by Chevron Chemical Co., Richmond, Calif.; CDL:229289-H). (00065494)

Ospenson, J.N. (1958) Letter sent to G.K. Kohn dated Feb. 4, 1958: Dibrom--
physical and chemical properties. Includes method dated Apr. 3, 1957.
(Unpublished study received Feb. 10, 1958 under unknown admin. no.; submitted
by Chevron Chemical Co., Richmond, Calif.; CDL:119717-A). (00074724)