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A STUDY OF INDUSTRIAL DATA ON CANDIDATE CHEMICALS FOR TESTING

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Research Request No. 2

FINAL REPORT

Office of Toxic Substances
U.S. Environmental Protection Agency
Washington, D.C. 20460

SRI International

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A STUDY OF INDUSTRIAL DATA ON CANDIDATE CHEMICALS FOR TESTING

by

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Chemical-Environmental Program

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CONTENTS

LIST OF TABLES

I. INTRODUCTION

A. Background

The Office of Toxic Substances of the Environmental Protection Agency needs to produce information packages as a basis for decisions about testing chemicals for unreasonable risk to human health or the environment. Contract No. 68-01-4109 with SRI International (formerly Stanford Research Institute) was established as a first step in producing these packages. It calls for SRI to provide, in answer to Research Requests provided by the Project Officer, selected economic, chemical, and biological information on selected commercial chemicals.

B. Objectives

The objectives of this study were to provide selected economic information on twelve chemicals of interest, designated by the Project Officer, in the form of a tabular summary and prepare market forecasts for each chemical.

II. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

A. Summary

This report describes the work carried out on Research Request No. 2 as specified by the Project Officer.

Data were collected on production and trade statistics, past and current uses, possible substitutes (including price information), and trends in production for twelve chemicals designated by the Project Officer. Some of these data appear in a concise tabular summary of the chemicals in alphabetical order, followed by market forecasts on each chemical, which include a complete discussion of all the information obtained in the study.

B. Conclusions and Recommendations

Because Research Request No. 2 was designed to provide certain specified information on selected chemicals, no conclusions were drawn from the studies performed, nor are any recommendations appropriate.

III. STUDY OF TWELVE CHEMICALS OF INTEREST TO EPA-OTS

A. Tabular Summary

The Project Officer requested a tabular summary of the twelve chemicals in alphabetical order using the chemicals names designated by EPA-OTS. This summary is presented in Table III-1. After each chemical name is listed the Chemical Abstracts Service Registry Number (CAS number), the most recent reported or estimated production level in millions of pounds and kilograms, the current price in cents per pound for large lots, and the total market value in millions of dollars (production level x price).

B. Market Forecasts

Market forecasts were prepared for each chemical and include a discussion of economic information requested by the Project Officer. The information presented for each chemical includes the following: production and trade statistics; a discussion of current uses, and in some cases, past uses; possible substitute products for the chemical in specific applications, and the current price of those substitutes; trends in production levels (i.e., future growth rates); and factors affecting growth in the market for the chemical.

These market forecasts follow Table III-1, and are presented in alphabetical order by chemical name.

Table III-1

TWELVE CHEMICALS STUDIED IN RESEARCH REQUEST NO. 2

Chemical Name	CAS Number	Year	Estimated Production: Millions of pounds	Estimated Production: Millions of kilograms	Current Price cents/lb.	Total Market Value Millions of dollars
1,5-Bis(chlorendo)cyclooctane	13560-89-9	1976	<17.3*	<8	170	<29
Bis(2-chloroethyl)ether	111-44-4	1976	>0.005	>0.002	9+	>0.00045
Bromoform	75-25-2	1976	>0.001	>0.000454	270 (pharmaceutical grade)	>0.0027
2-Chloroethanol	107-07-3	recent years	30	13.6	ND	--
Diethyl N,N-bis(2-hydroxyethyl)-aminophosphonate	2781-11-5	1977	4-8*	1.8-3.6	88	3.5-7.0
N-1,3-Dimethylbutyl-N-phenyl-p-phenylenediamine	793-24-8	1976	36	16.4	187-190 flakes:197-200	68.4
4-Methyl-7-diethylamino-coumarin	91-44-1	1976	0.085	0.0386	850 (crude)	0.72
Sodium fluoride	7681-49-4	1972	12.3	5.6	31-32 114 (USP grade)	3.8-3.9
Sodium fluorosilicate	16893-85-9	1976	114.1	51.9	12-13	13.7-14.8
Stannous chloride	7772-99-8		ND	ND	469 (anhydrous) 490 (hydrated)	-- --
Vinyl pyridine	1337-81-1					
2-Vinyl pyridine		1976	4.5	2.0	159	7.2
4-Vinyl pyridine		1976	>0.005	>0.002	314	>0.016
Vinyl pyrrolidone	88-12-0	1974	10-12	4.5-5.5	97	9.7-11.6

* Consumption
+ Price quoted in 1971 (most recent available figure)
ND= No data

1,5-Bis(chlorendo)cyclooctane is a chlorinated cycloaliphatic flame retardant additive used in plastics. It is believed to be commercially marketed in the U.S. by one company as one of several chemicals covered by the tradename Dechlorane®. Although the producing company has not divulged the chemical structure of the compounds marketed in the Dechlorane® product line, a survey of the literature indicates that the adduct of 2 moles of hexachlorocyclopentadiene + 1 mole of 1,5-cyclooctadiene, i.e., 1,5-bis(chlorendo)cyclooctane has the same physicochemical properties as the commercially available product, Dechlorane® 25 (also known as Dechlorane® Plus 25), and probably has the same structure.

Information on U.S. production of Dechlorane® 25 is not available from the U.S. International Trade Commission. Industry sources estimate that 35.2 million lbs. (16 million kg) of "chlorinated paraffins and cycloaliphatics" (including Dechlorane® 25) were used as flame retardant additives in 1977, and 33 million lbs. (15 million kg) in 1976.[1] Chlorinated paraffins used as flame retardant additives generally contain at least 65% chlorine. U.S. production of chlorinated paraffins containing >65% chlorine combined with those containing <35% chlorine was reported to have been 15.7 million lbs. (7.1 million kg) in 1976.[2] It is believed that chlorinated paraffins containing >65% chlorine make up the bulk of this class. Therefore, subtracting the assumed 15.7 million lbs. of chlorinated paraffins produced in 1976 from the total estimated 33 million lbs. of chlorinated paraffins and cycloaliphatics used in 1976, indicates that as much as 17.3 million lbs. (8 million kg) of chlorinated cycloaliphatics, including Dechlorane® 25 could have been used as flame retardants in plastics in 1976. U.S. imports and exports data for Dechlorane® 25 are not available.

Dechlorane® 25 is added, commonly in combination with inorganic fillers (especially antimony trioxide), to polymers to impart flame retardancy. It is widely used in polypropylene (especially in wire and cable and UL-94 applications which cover parts and devices in appliances). Other polymers in which it is reportedly consumed include ABS, acrylic, epoxy, and phenolic resins, nylon, polyester, polyethylene, polystyrene, polyvinyl acetate, and polyvinyl chloride.[3]

Because flame retardant additives affect the processing properties of the polymer, selection of a specific additive for a specific plastic depends upon the properties required by a particular polymer system. The selection of substitutes for Dechlorane® 25, therefore, depends not only on cost and flame retardant performance, but also on the specific polymer processing conditions. Possible substitutes for Dechlorane® 25 reported in the trade literature, the polymers in which they are used, and their prices are listed in Table III-2.[1,3]

Table III-2

Possible Substitutes for Dechlorane® 25

Product	Applicable Polymers	Price (cents/lbs)[4]
Chlorinated parraffins, for example:	ABS; acrylics, epoxy, nylon; phenolic; polyester; polyolefins; polystyrene; polyvinyl acetate; polyvinyl chloride	
Chlorowax 70		45.5
Chlorowax 70S		49.5
Halorex 70S		49.5
Citex BC-26	ABS; acrylics, polypropylene; polystyrene; polyvinyl acetate	190
Citex BT-93	Polypropylene; impact-modified polystyrene	175
Great Lakes DE-83R (decabromodiphenyloxide)	ABS; epoxy; phenolic; polyester; polyolefins; polystyrene; polyvinyl acetate; polyvinylchloride	132-140
Hi Flame-Out 103 (trichlorotetrabromotoluene) Hi Flame-Out 104 (pentabromophenylbenzoate) Hi Flame-Out 105 (pentabromoethylbenzene)	ABS; polyester; polyolefins for wire and cable; polystyrene	150
Pyro-Chek 77B	Nylon; polyolefins	150

Although the company which produces Dechlorane ® 25 has already eliminated one product from the Dechlorane ® line due to government regulations on its effluent discharges into waterways, as of late 1977, it planned to continue producing Dechlorane ® 25. Dechlorane ® 25 availability has, however, been limited recently due to the shut-down of a hexachlorocyclopentadiene production plant resulting in customer allocation based on 70% of 1976 usage. The projected 1977-1982 growth rate for products such as Dechlorane ® 25 is estimated at 3-5% per year by industry sources.[5]

BIS(2-CHLOROETHYL)ETHER

Bis(2-chloroethyl)ether was formerly produced as a by-product of the ethylene chlorohydrin route to ethylene oxide. The chlorohydrin route was the main method of ethylene oxide manufacture until 1957. As companies began using direct ethylene oxidation, production via the chlorohydrin route declined and dropped to zero in 1973 and 1974. One U.S. company did resume production of ethylene oxide via the chlorohydrin route in 1975 and 1976 due to unusual circumstances, however, this situation is not expected to recur in the future.

U.S. production figures for bis(2-chloroethyl)ether were last reported in 1960 and amounted to 26.6 million lbs. (12 million kg), with sales amounting to 15.4 million lbs.[6] U.S. sales during 1961-1965 were reported as follows:[7-11]

Year	Sales (millions of lbs.)
1961	8.9
1962	7.3
1963	11.8
1964	8.8
1965	2.0

Two companies reported commercial production of bis(2-chloroethyl)ether to the U.S. International Trade Commission during 1966-1969, and only one company reported it during 1970-1973 and in 1976. Commercial production was not reported in 1974 and 1975. Since only one U.S. company reported commercial production of bis(2-chloroethyl)ether in 1976, this indicates that at least 5,000 lbs. (2,272 kg) or $5,000 worth of bis(2-chloroethyl)ether were produced.[2] One other company is also believed to be producing bis(2-chloroethyl)ether in the U.S.; however, no data are available on its production capacity.

No evidence was found to indicate that bis(2-chloroethyl)ether is currently marketed commercially in the U.S. It is believed that the producing companies consume it internally as a solvent in chemical processes and as a chemical intermediate for the production of proprietary products. Data on U.S. imports and exports of bis (2-chloroethyl)-ether are not available.

Since bis(2-chloroethyl)ether is used in proprietary processes by the producing companies, no information is available to describe the specific end-uses that are in current practice. In the past, it has been used in a variety of applications described as follows: as a solvent for fats, waxes, and grease; as a scouring agent for textiles to remove paint and tar brand marks from raw wool and oil and grease spots from cloth; as a chemical intermediate in the production of alkyl aryl ether sulfate or sulfonate type anionic surface-active agents (which have been used in kier-boiling, desizing, and scouring operations, as emulsifiers in cosmetics, as detergents and lathering agents in shampoo and cleansing cream bases, and in metal cleaning operations); as a solvent for the separation of butadiene from butylene; in the synthesis of morpholine and N-substituted morpholine derivatives (N-hexadecyl morpholine); as a chemical intermediate in divinyl ether synthesis; as a chemical intermediate in the manufacture of resins and plasticizers, textile chemicals, pharmaceuticals, insecticides, rubber chemicals, and lubricating oil additives; in a mixture with nitrobenzene for use as a solvent in the fractionation of wax-containing mixtures; as a component of anti-knock compounds (lead scavenger); as a selective solvent in the production of high-grade lubricants and other naphthenic crude oils; as an insecticide sprayed on corn silk to control earworms; and as a soil fumigant.[12-13]

A discussion of specific substitutes for bis(2-chloroethyl)ether in its current applications is not possible, due to the proprietary nature of its usage. Although data are not available to quantitatively assess or forecast the U.S. market for bis(2-chloroethyl)ether, it appears that because of the chemical's limited usage, future consumption will remain static or continue to decline. If ethylene oxide production via the chlorhydrin route is permanently discontinued under all circumstances, future production levels of bis(2-chloroethyl)ether will probably be very small, since it will no longer be available as a byproduct.

Only one U.S. company reports commercial production of bromoform to the U.S. International Trade Commission. This implies that a minimum of 1,000 lbs. (454 kg) or $1,000 worth of bromoform is produced annually in the U.S.[2] Data on U.S. imports and exports of bromoform are not available.

Although bromoform is classified under the Medicinal section -- "General Antiseptic and Antibacterial Agents" -- by the U.S. International Trade Commission, no evidence was found to indicate that it is actually used for those applications. Bromoform had been used in the past as an antitussive/sedative for the treatment of whooping cough and seasickness.[14]

Because the market for bromoform is relatively small, little information is available on its end uses. Bromoform is believed to be used as a chemical intermediate for the manufacture of pharmaceuticals; in geological assaying for the separation of minerals; as an ingredient in fire-resistant chemicals and gauge fluids; as a solvent for waxes, greases and oils; and as an intermediate in organic synthesis.[15-16]

No information is available to form a basis for discussion on bromoform substitutes. No data is available to quantitatively assess the future growth of the U.S. bromoform market. However, because the market is small and specialized, it would appear likely that the market for bromoform will remain relatively static.

2-Chloroethanol, more commonly known as ethylene chlorohydrin, is a chemical intermediate that has been used for the production of many chemicals. Prior to 1972, 2-chloroethanol was produced in large quantities (200-500 million lbs.) (90-227 million kg) as an unisolated intermediate in the production of ethylene oxide. This production dropped to zero in 1973 and 1974 when the chlorohydrin route to ethylene oxide became economically unattractive. However, in 1975 and 1976, one U.S. company did produce significant quantities (about 50 million lbs. or 23 million kg) of 2-chloroethanol for use as an unisolated intermediate for ethylene oxide production due to unusual circumstances. This situation is not expected to resume in the future so that all U.S. ethylene oxide production will be derived by direct oxidation of ethylene. Since only one U.S. company reported production of 2-chloroethanol in 1976, production data are not available from the U.S. International Trade Commission.[2] However, based on the estimated quantity of ethylene oxide (derived from direct oxidation of ethylene) used to produce 2-chloroethanol in recent years (probably by reaction with a metal chloride), an estimated 30 million lbs. (13.6 million kg) of isolated 2-chloroethanol has been available. However, the one U.S. company which reported production in 1976 has apparently discontinued production of 2-chloroethanol since then.

U.S. imports of 2-chloroethanol amounted to 2,200 lbs. (1,000 kg) in 1976 (from Japan), 1.8 million lbs. (0.8 million kg) in 1975 (over 96% from Japan), and 2,200 lbs. (1,000 kg) in 1974 (from unspecified countries).[17-19] Data on U.S. exports are not available.

2-Chloroethanol is used as a raw material along with formaldehyde to produce bis(2-chloroethyl)formal which is used to produce polysulfide elastomers (used in printing rollers, hose, and gaskets where solvent resistance is critical).[20] 2-Chloroethanol reportedly can also be used as a chemical intermediate for anthraquinone dyes, β-phenylethanol (synthetic oil of rose), choline (a B vitamin essential for egg production in chickens), and a variety of other types of specialty chemicals. It is used primarily to introduce a hydroxyethyl group into other organic compounds.[21]

Due to the limited market for 2-chloroethanol, information on specific substitutes is not readily available. It is believed that about 95% of commercially available polysulfide polymers are based on the bis(2-chloroethyl)formal derived from 2-chloroethanol. Ethylene dichloride is also used in polysulfide elastomers as well as small amounts of 1,2,3-trichloropropane, bis(4-chlorobutyl)ether, and bis(4-chlorobutyl) formal, however, bis(2-chloroethyl)formal appears to be a necessary component for polysulfide polymers.[20]

Industry sources estimate that future consumption of ethylene oxide for the production of 2-chloroethanol will not exceed an annual average growth rate of 8.5% through 1983.[22]

DIETHYL N,N-BIS(2-HYDROXYETHYL)AMINOMETHYLPHOSPHONATE

Diethyl N,N-bis(2-hydroxyethyl)aminomethylphosphonate is a reactive polyol used in the production of flame retardant rigid polyurethane foam. It is commonly known by its trade name, Fyrol® 6. Since only one company produces it in the U.S., production data are not available from the U.S. International Trade Commission. Industry sources estimate that 15.4 million lbs. (7 million kg) of "urethane intermediates (rigid foam)" (including Fyrol ® 6) were used as flame retardants in the production of rigid polyurethane foam in 1977, an increase of 16.7% from 1976 consumption levels.[1] It is estimated that Fyrol® 6 accounts for about 4-8 million lbs. (1.8-3.6 million kg) of that market. Data on U.S. imports and exports of Fyrol ® 6 are not available.

Fyrol ® 6 is widely used in flame retardant rigid polyurethane foams at levels of 5 to 15%, where it reacts as a polyol and replaces part of the polyether in the foam formulation.[2,3] Rigid polyurethane foams are primarily used as insulating material in construction, refrigerators and freezers, and truck and trailer bodies. They are also used in the manufacture of ornamental trim molding for furniture. Flame retardant rigid polyurethane foams are particularly important in the building and construction industry.

A number of other reactive flame retardants are commercially available for use in rigid polyurethane foams. Some mentioned in the trade literature are included in Table III-3.[3]

Table III-3

Possible Substitutes for Diethyl N,N-bis(2-hydroxyethyl)aminomethylphosphonate

Compound	Price (cents/lb.)[4]
Brominex 257	70
Chlorendic anhydride (HET Acid and Anhydride)	82
2,3-Dibromo-2-butene-1,4-diol	not available

Table III-3 (Continued)

Compound	Price (cents/lb.)[4]
Dibromobutendiol acetate	not available
Dibromoneopentyl glycol (FR-1138)	not available
Di-(polyoxyethylene)hydromethyl-phosphonate (Fyrol HMP)	260
Tetrachlorophthalic anhydride (Tetrathal)	72
Thermolin RF-230	75
Tribromoneopentyl alcohol (FR-1360; FR-2249)	not available
Vircol 82	78

Many new reactive flame retardants are reportedly under development by the industry. Selecting a specific substitute for Fyrol® 6 would be dependent upon the specific cost/performance characteristics exhibited by other products as well as the processing conditions required for its application.

Future growth in the usage of reactive flame retardants for rigid polyurethane foams, including Fyrol® 6, will depend upon the building and construction codes set for the industry. The projected 1977-1982 growth rate for products such as Fyrol® 6 is estimated at 6-10% per year by industry sources.[5]

N-1,3-DIMETHYLBUTYL-N-PHENYL-P-PHENYLENEDIAMINE

N-1,3-Dimethylbutyl-N-phenyl-p-phenylenediamine is used as an antioxidant and antiozonant in rubber processing. U.S. production of this chemical reported to the U.S. International Trade Commission amounted to 37.5 million lbs. (17 million kg) in 1974 and 30.5 million lbs. (13.9 million kg) in 1975.[24-25] Although three companies reported production in 1976, a separate production figure was not reported.[2] Since it accounted for about 50% of the total production reported for the class "substituted p-phenylenediamines" in 1974 and 1975, and production of the class was 71.78 million lbs. in 1976, production of this chemical in 1976 is estimated to have been about 36 million lbs. (16.4 million kg). U.S. imports of N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine through principal U.S. customs districts in recent years were reported as follows:[26-29]

Year	Quantity (lbs.)
1973	287,636
1974	117,563
1975	258,380
1976	380,506

Data on U.S. exports of N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine are not available.

N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine is a protective additive compounded into rubber to provide resistance to ozone, fatigue, and aging degradation under static and dynamic conditions. It is recommended for use as an antiozonant and antioxidant in rubber based on isoprene (natural and synthetic), butadiene, and styrene-butadiene, particularly for protection against crack formation and crack growth. It is also used to inhibit degradation caused by copper and manganese contaminants. Major types of rubber products employing N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine include carbon black-filled tires and mechanical goods.[30]

Selection of a specific substitute for N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine depends upon the specific properties of the potential antiozonant, as well as cost/performance considerations.

Since most antiozonants are generally also useful as antioxidants but many antioxidants do not possess the ability to protect against ozone degradation, antiozonant properties are the most important consideration in choosing a substitute. The specific properties of a substitute which would have to be considered include volatility, solubility, chemical stability, physical state, and toxicity. In addition, specific types of antiozonants are only compatible with certain types of rubber.[31] Some possible substitutes for N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine are listed in Table III-4.[30]

Table III-4

Possible Substitutes for N-1,3-dimethylbutyl-N-phenyl-p-phenylenediame

Compound	Price* (cents/lb.)
N,N'-Bis(1,4-dimethylpentyl)-p-phenylenediamine (Flexzone 4L; Santoflex 77)	179-182
N,N'-Bis(1-ethyl-3-methylpentyl)-p-phenylenediame (Flexzone 8L)	179-182
Blend of alkyl & aryl derivatives of p-phenylenediamine (Flexzone 10L; Flexzone 11L; Flexone 12L)	183-190
1/1/1 Blend of dioctyl-, phenylhexyl-, and phenyloctyl-p-phenylenediamine (Anto[3] C)	184-187
Diheptyl-p-phenylenediamine (Anto[3] G)	179-182
N,N'-Di-3(5-methylheptyl-p-phenylenediamine) (Antozite 2)	181-184
Dioctyl-p-phenylenediamine (Anto[3] D; Antozite 1)	174-177
6-Ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (Santoflex AW)	129-132
N-Isopropyl-N'-phenyl-p-phenylenediamine (Flexzone 3-C; Santoflex IP)	193-196
Phenyl, hexyl-p-phenylenediamine (Anto[3] E)	197-200
Phenyl, octyl-p-phenylenediamine (Anto[3] F)	187-190

* Taken from November, 1977 issue of "Rubber World"

Although the market for rubber processing chemicals such as N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine is believed to have grown by about 10% in 1977, prospects for long-term growth are relatively poor. Growth in this market is tied to growth in U.S. rubber consumption, and industry sources expect U.S. rubber consumption to grow at only about 3% per year, with tire consumption (the most important market for N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine) growing by as little as less than 2% per year. This outlook results from the move to smaller cars; smaller tires; radial tires; and lowered speed limits. Some new growth may occur in the market for rubber processing chemicals as a result of the shift to more durable tires, which will consume larger amounts of processing chemicals to meet higher performance requirements.[32]

4-Methyl-7-diethylaminocoumarin is an optical brightener used primarily in the textile and detergent industries to increase the whiteness and brightness of fibers and clothes. Since only two companies reported commercial production of crude 4-methyl-7-diethylaminocoumarin to the U.S. International Trade Commission in 1976, separate production figures are not available. However, based on reporting minimums established by the commission, 1976 U.S. production of this chemical exceeded 10,000 lbs. (4,500 kg) or $10,000 in value.[2]

The Society of Dyers and Colourists has classified all the optical brighteners developed for use in the textile industry, and the U.S. International Trade Commission reports production of specific brighteners based on their nomenclature. Although the specific brighteners are numbered (e.g., Fluorescent Brightening Agent 55), the Society of Dyers and Colourists does not disclose the chemical identity of each agent, revealing only the general chemical class to which it belongs (e.g., aminocoumarin). Based on evidence discovered in the literature, it appears that 4-methyl-7-diethylaminocoumarin is the major component of Fluorescent Brightening Agent 61.[33-35] U.S. production of Fluorescent Brightening Agent 61 amounted to 33,000 lbs. (15,000 kg) in 1975 and 85,000 lbs. (38,600 kg) in 1976.[2,25] It is not known whether 4-methyl-7-diethylaminocoumarin is a component of any other fluorescent brightening agents. Data on U.S. imports and exports of either 4-methyl-7-diethylaminocoumarin or Fluorescent Brightening Agent 61 are not available.

4-Methyl-7-diethylaminocoumarin is used as an optical brightener by the textile industry for wool, nylon, and acetate fibers, and as an ingredient in fine-fabric laundering compositions which are not used in the presence of chlorine bleach.[36-38] It is also used as an optical brightener in pigmented coatings and solvent and water-based coatings.[39] 4-Methyl-7-diethylaminocoumarin is an important laser dye standard in the blue and green region of the spectrum; however, the laser grade is very expensive and only a few milligrams are required for its use.[40]

Other reported uses for 4-methyl-7-diethylaminocoumarin which could not be verified as being commercial include: as an optical brightener for paper, labels and book covers; to lighten plastics and resins; and as an invisible marking agent.[16] One U.S. patent describes a potential use in a fluorescent skin-marking composition for animals and humans to indicate areas of skin to be subjected to radiation therapy.[33]

A reference text on optical brighteners has reported that although brighteners with better properties have been developed, products containing 4- methyl-diethylaminocoumarin are still in common usage.[41] In 1976, 4-methyl-7-diethylaminocoumarin is estimated to have accounted for less than 0.2% of the total reported U.S. production of optical brighteners (43.4 million lbs. or 19.7 million kg).[2] Almost 300 fluorescent brighteners have been developed, of which the most important compositions cover at least 14 different structural types: 4,4-bis-(triazinylamino)-stilbene-2,2'-disulfonic acids; 4,4-bis-(v-triazol-2-yl)-stilbene-2,2'-disulfonic acids; 4,4'-bis-(diphenyltriazinyl)-stilbenes; 4,4'-distyryl-biphenyls; 4-phenyl-4'-benzoxazolyl-stilbenes; stilbenyl-naphthotriazoles; 4-styryl-stilbenes; bis-(benzoxazol-2-yl)-derivatives; bis-(benzimidazol-2-yl)-derivatives; coumarins; pyrazolins; naphthalimides; triazinyl-pyrenes; and 2-styryl-benzoxazoles and naphthoxazoles.[37] Of the 19 fluorescent brightening agents specifically listed as being commercially produced in the U.S. in 1976 by the U.S. International Trade Commission, nine compositions have applications similar to 4-methyl-7-diethylaminocoumarin. These brighteners are listed in Table III-5 as possible substitutes.[34,39]

Table III-5

Possible Substitutes For 4-Methyl-7-diethylaminocoumarin

Fluorescent Brighteners	Chemical Class	Textile Uses Applicable to 4-Methyl-7-diethylamino-coumarin	Price (cents/lb.)[4]
25 (Blancophor SV)	Stilbene	Wool	342
28 (Calcofluor White PMS, PMW, ST)	4,4'-Bis((anilino-6-(bis(2-hydroxy-ethyl(amino)-s-triazin-2-yl) amino)-2,2'-stilbenedisulfonic acid	Nylon; laundry formulations	84
49 (Leucophor BS)	Bistriazinyl-aminostilbene	Nylon	120
52 (Leucophor WS; Leucopur Base)	Coumarin derivative	Acetate; nylon	120
54 (Tinopal WG)	Not known	Nylon	not available
59 (Tinopal RBN)	Stilbene-triazole sulfonic acid derivative	Nylon	not available
125 (Calcofluor White EDW, PUM)	Triazinylstilbene derivative	Nylon	not available
130 (Calcofluor White LD)	Coumarin derivative	Wool, nylon, acetate, detergent formulations	1100
134 (Uvitex CF)	Stilbene	Nylon, wool	not available

No information was available on which to forecast the future growth of 4-methyl-7-diethylaminocoumarin production in the U.S.

Four companies are currently believed to be producing commercial quantities of sodium fluoride in the U.S. Production figures for sodium fluoride are not available; however, based on hydrofluoric acid consumption for the production of fluoride salts, sodium fluoride production is estimated to have been less than 13 million lbs. (6 million kg) in 1976. In 1972, the U.S. Bureau of the Census reported production of 12.3 million lbs. (5.6 million kg) of sodium fluoride.[42] Data on U.S. imports and exports of sodium fluoride are not available.

Sodium fluoride was primarily used in the past for the fluoridation of municipal drinking water supplies; however, it has been replaced by most communities with hydrofluosilicic acid and sodium fluorosilicate which are much cheaper. Very small communities may still be using it because it is easy to handle.

Sodium fluoride is also used in the following applications: in the pickling of stainless steel to remove scale; in exothermic mixtures (heat producing materials) to keep molten metal from solidifying, e.g., during the casting of iron, steel, or aluminum; as a fluxing agent in aluminum resmelting to clean and cover the metal and to modify or grain refine the metal structure; for the surface treatment of metals to obtain a satin finish; as a degassing agent in the manufacture of rimmed steel; as a frosting agent in glass manufacture; as a preservative in casein, glue, and starch adhesives; and as a dental caries prophylactic (in tablet, liquid, capsule, and gel form).[43-45] Other reported uses for sodium fluoride include use as an antiseptic in breweries and distilleries; in heat treating salts; and in the manufacture of coated papers.[46]

Sodium fluoride has been used as a component of wood preservatives for protection against fungal rot and decay used for mine timbers, pilings, posts, poles, and other wood structures and in insecticide compositions for cockroaches, ants, silverfish, centipedes, crickets, spiders, sowbugs, and termites. It is not known whether it is still being used for all of these applications.[47]

In general, applications for sodium fluoride can be served by other fluoride compounds. Possible substitutes for sodium fluoride are listed in Table III-6. All of these chemicals are used in the applications described, and in some cases are consumed to a greater extent than sodium fluoride.[43]

Table III-6

Possible Substitutes for Sodium fluoride

Compound	Application	Price[48] (cents/lb.)
Fluorspar	Fluxing agent in aluminum resmelting	4.8-5.0 (value)
Hydrofluoric acid	Pickling stainless steel; frosting glass; metal surface treatment to obtain satin finish	33.8 (70% basis)
Hydrofluosilicic acid	Water fluoridation	3.75 (23% basis)
Potassium fluoroborate	Fluxing agent in aluminum resmelting	37½ - 49
Sodium fluoroborate	Fluxing agent in aluminum resmelting	40½ - 46
Sodium fluorosilicate	Water fluoridation; in exothermic mixtures to keep molten metal from solidifying	12 - 13

Because sodium fluoride is an expensive chemical, relative to other fluorides, demand has been declining due to the availability of cheaper substitutes. It is not known whether this decline has levelled off or is still falling; however, prospects for market growth are dim.

SODIUM FLUOROSILICATE

Six companies produce commercial quantities of sodium fluorosilicate in the U.S. U.S. production figures reported by the U.S. Bureau of the Census in recent years are as follows:[42,49]

Year	Production (million lbs.)
1976	114.1
1975	97.0
1974	103.2
1973	108.0
1972	114.7
1971	120.8

U.S. imports of sodium fluorosilicate amounted to 12.0 million lbs. in 1976, 18.3 in 1975, 15.4 in 1974, and 9.4 in 1973.[17-19,50] Data on U.S. exports of sodium fluorosilicate are not available.

Sodium fluorosilicate is primarily used for the fluoridation of municipal drinking water supplies by small communities which do not want to invest in the liquid metering equipment necessary for the use of hydrofluosilicic acid. Sodium fluorosilicate has numerous other uses including the following: as a flux in aluminum refining; in exothermic mixtures (heat producing materials) to keep molten metal from solidifying; as an opacifier in the production of opal glass; as a constituent of vitreous enamel frits where it acts as a flux during smelting and contributes greater opacity in the final enamel coating; in enamel glazes for chinaware; in the metallurgy of beryllium and zirconium; as a laundry scouring agent; in the manufacture of acid-resistant cement; in lead refining; as a gelling agent for natural isoprene rubber latex foam; as a mothproofing agent for woolen fabrics, carpets, feathers, and furs; as a preservative to prevent mold in glue, starch sizes and leather processing; as a slime control agent in paper manufacture; as a rodent repellent in paperboard shipping containers; and as an insecticide for earwigs, cutworms, sowbugs, strawberry root weevil, ants, centipedes, cockroaches, crickets, and silverfish.[30,43-44,47]

In general, applications for sodium fluorosilicate can be served by other fluoride compounds. Possible substitutes are listed in Table III-7.[30,43] All of these chemicals are used in the applications described, and in some cases are consumed to a greater extent than sodium fluorosilicate.

Table III-7

Possible Substitutes for Sodium Fluorosilicate

Compound	Application	Price (cents/lbs)[48]
Ammonium nitrate	Gelling agent for natural isoprene rubber latex foam	4.5 - 5.75 (33.5% basis)
Ammonium sulfate	Gelling agent for natural isoprene rubber latex foam	3 - 4.5
Diphenylguanidine	Gelling agent for natural isoprene rubber latex foam	182 - 192
Di-ortho-tolyguanidine	Gelling agent for natural isoprene rubber latex foam	117 - 120
Fluorspar (metallurgical and acid grade)	Flux in aluminum refining; opacifier in production of opal glass	4.8-5.0 (value)
Hydrofluosilicic acid	Fluoridation of municipal water supplies	3.75 (23% basis)
Potassium fluorosilicate	Flux for vitreous enamel frits	11.5 - 15
Sodium fluoride	Fluoridation of municipal water supplies; in exothermic mixtures to keep molten metal from solidifying	31 - 32

Information is not available on which to base a quantitative forecast of the future growth in sodium fluorosilicate production. An important factor in the future consumption of sodium fluorosilicate will be the future status of municipal water fluoridation programs, the safety of which has been under review by the Food and Drug Administration.

No information was available to indicate the size of the U.S. stannous chloride market. Only two companies produce commercial quantities of stannous chloride in the U.S. It is available in anhydrous and hydrated forms.

Stannous chloride is primarily used in metal plating applications. It is believed that about 70% of U.S. stannous chloride consumption is used in the electrotinning of steel strip via the halogen process. In simple terms, steel strip is tinplated by electrolytically oxidizing metallic tin (the anode) in an electrolytic plating solution to cause metallic tin to be deposited on the steel strip (the cathode) moving through plating unit. In the halogen process the plating bath electrolyte consists of an aqueous solution of stannous chloride and alkali metal fluorides. There are two other tinplating processes which are commonly used; one uses a plating bath electrolyte containing a solution of stannous sulfate and phenolsulfonic acid, and the other uses an electrolyte based on a solution of sodium stannate and sodium hydroxide.[51] Tinplated steel strip is used primarily in the manufacture of metal cans, especially for the food industry. The steel provides container strength and the tinplate provides resistance to corrosion.

Stannous chloride is also used in tin-nickel plating (65% tin and 35% nickel). These coatings are used for printed circuit boards, watch parts, drawing instruments, scientific apparatus, refrigeration equipment, musical instruments, and handbag frames.[52]

Stannous chloride is also used in numerous other applications including the following: as a sensitizer for the silvering of plastics and mirrors; in a tin coating for sensitized paper; as an intermediate for tin chemicals manufacturing; as an antisludge agent for oils; as an additive to drilling muds; as a soldering flux; as a food additive to protect and enhance flavors, prevent corrosion, and maintain food colors in canned food, especially in carbonated soft drinks (at levels of 11 ppm), and also for asparagus (20 ppm) and other foods (15 ppm); as a tanning agent for leather; as a stabilizer for perfumes in toilet soaps; as a mordant in printing dyes; as an antioxidant; as a catalyst in organic reactions (e.g., it has been used with phenolic resins to cure butyl rubber); as a reducing agent in laboratory procedures (e.g., in the preparation of aryldichlorostibines by reduction of the corresponding stibonic acid in hydrochloric acid solution); as an analytical reagent; and in the manufacture of pigments and pharmaceuticals.[53-57]

Selecting a substitute for stannous chloride in its most important application, tinplating, would depend on the cost/performance characteristics of other plating processes. As described previously, other tinplating processes are in common usage which use electrolytes that are not based on stannous chloride. Other types of steel which resist corrosion are also available, primarily, tin-free steel in which chromium is electrolytically plated on black plate steel or blackplate steel coated with suitable organic coatings.[51] Aluminum cans are making inroads into the major market for tinplated steel, metal cans, primarily in beverage container applications.[58]

Consumption of tin for use in chemicals such as organotin compounds and inorganics, including stannous chloride, has grown at an average annual rate of 8.5% since 1970, according to the U.S. Department of Commerce, and will grow by 5% in 1978. Shipments of metal cans (major market for tinplate) are expected to grow by 2.2%/year reaching 97 billion cans by 1982, with beverage cans accounting for most of the growth. By 1980, aluminum cans are expected to account for 75% of the beverage can market. The use of all metal cans could be adversely affected by legislation restricting the use of nonreturnable beverage containers.[58]

Vinyl pyridine is commercially available in the U.S. in the form of two isomers, 2- and 4-vinyl pyridine. Since only one U.S. company reports commercial production of 2- and 4-vinyl pyridine, production data are not available from the U.S. International Trade Commission. Virtually all the U.S. production of 2-vinyl pyridine is used in the production of styrene-butadiene-vinyl pyridine terpolymer elastomers. Based on industry-wide usage of about 15 wt. % 2-vinyl pyridine in these products, U.S. consumption of 2-vinyl pyridine is estimated at 4.5 million lbs. (2 million kg) in 1976. U.S. production of 4-vinyl pyridine (based on U.S. International Trade Commission reporting minimums) exceeds 5,000 lbs. (2,272 kg) or $5,000 in sales value.[2] Data on U.S. imports and exports of 2- and 4-vinyl pyridine are not available.

Almost all U.S. consumption of 2-vinyl pyridine is used to produce styrene-butadiene-vinyl pyridine elastomer latex. The latex is used in an adhesive dip along with a resorcinol and formaldehyde resin (11 parts resorcinol to 6 parts formaldehyde). The dip usually contains 17 parts resorcinol-formaldehyde resin and 100 parts latex and is used to bond nylon, rayon, polyester, and fiberglass (or other fibers or textile fabrics) to rubber; these cord- or fabric-reinforced rubber products include tires (major market), industrial belting, and V-belts. Rayon fibers only require a latex containing about 50% of the vinyl pyridine terpolymer, with the rest made up of styrene-butadiene copolymer latex. Nylon fibers require 75-100% vinyl pyridine terpolymer in the latex, and polyester and fiberglass dips contain 100% vinyl pyridine terpolymer in the latex. Polyester fibers also require either: (1) addition of a proprietary modified resorcinol-formaldehyde resin to the adhesive dip; or (2) a two step process in which the fibers are first dipped in a reactive polymer based on a mixture of isocyanates and epoxy resins followed by dipping in the conventional resorcinol-formaldehyde-latex dip.

U.S. production of styrene-butadiene-vinyl pyridine elastomer dropped from a high of 38.2 million lbs. (17.3 million kg) in 1972 to 29.8

million lbs. (13.6 million kg) in 1976, a decrease of 22%.[2,59] This decline is primarily a result of increased usage of steel-belted tires, which uses different rubber processing technology and does not consume styrene-butadiene-vinyl pyridine elastomer latex. Another factor contributing to the decline is increased usage of polyester tire cord which requires less of the styrene-butadiene-vinyl pyridine elastomer latex dip than the older nylon and rayon cords. It is believed that the decline in styrene-butadiene-vinyl pyridine elastomer consumption has bottomed out and will remain at the 1976 level through 1985. Therefore, production of 2-vinyl pyridine is expected to remain at about 4.5 million lbs. per year during that time period.

Although styrene-butadiene latex is also used to some extent in rayon and nylon bonding, the vinyl pyridine terpolymer latex appears to be necessary for tire performance.

Other reported uses specifically mentioned for the 2-isomer of vinyl pyridine include: (1) as an intermediate, via addition of methanol, to 2-β-methoxyethylpyridine (methyridine) used as a sheep and cattle anthelmintic; (2) as a dye assistant incorporated into acrylic fibers at levels of less than 5% of the polymer to promote acid dyeing (2-methyl-5-vinyl pyridine is also reportedly used); and (3) polymerization to polyvinyl pyridine for use as an element in photographic film.[60-61]

The market for 4-vinyl pyridine has not been well defined. It has reported use: (1) as a textile dyeing assistant for synthetic fibers under acid dyeing conditions; (2) for the preparation of copolymers with styrene and acrylonitrile; (3) in the manufacture of synthetic elastomers and photographic chemicals; (4) as a starting material for the synthesis of pyridine derivatives; (5) as a comonomer for the production of polyelectrolytes used in ion exchange resins and as flocculants and emulsifiers; and (6) in the preparation of polyvinylpyridium salts which are used as flocculants. (2-Vinyl pyridine has also been mentioned for use in the applications listed above.)[62-64]

No information was available on which to forecast the future growth of 4-vinyl pyridine production in the U.S.

VINYL PYRROLIDONE

Vinyl pyrrolidone is used as a monomer and as a chemical intermediate. Since only one company produces it in the U.S., production data are not available from the U.S. International Trade Commission. U.S. consumption of vinyl pyrrolidone (based on acetylene usage) is estimated to have been 10-12 million lbs. (4.5-5.5 million kg) in 1974. U.S. imports of vinyl pyrrolidone and its homopolymer, polyvinyl pyrrolidone combined amounted to 1.6 million lbs. (0.7 million kg) in 1976 and were from the Federal Republic of Germany (95%), France (2.5%), the German Democratic Republic (2.2%), and Sweden (0.3%).[17] Data on U.S. exports of vinyl pyrrolidone are not available.

Vinyl pyrrolidone is used primarily as a monomer for the manufacture of its homopolymer, polyvinyl pyrrolidone. Polyvinyl pyrrolidone is a unique polymer used in many industrial applications due to its wide range of properties as a film-former, adhesive, protective colloid, dispersant, stabilizer, binder, complexing agent and detoxicant. It is used in a wide variety of industrial and consumer products including: cosmetics (hairwave sets, aerosol hair sprays, shampoo, make-up, etc.); soaps and detergents; adhesives; ball-point pen and printing inks; paints and varnishes; paper and paper coatings; textile processing chemicals; printing plates; agricultural formulations; antifreeze sprays; and waxes and polishes. Polyvinyl pyrrolidone is used in pharmaceutical applications as a: tablet coating agent and binder; blood plasma extender for emergency use; tablet disintegrator; detoxifier; antidiarrhea agent; in injections, topical applications, and medicinal aerosols; and as a dialyzing medium. Polyvinyl pyrrolidone is also used as a beverage clarifier and stabilizer in beer, wine, whiskey, vinegar, fruit juices, and tea.[65-67]

Copolymers are made using vinyl pyrrolidone (usually at a concentration of 1-20%) with many other comonomers (e.g., vinyl acetate, ethyl acrylate, and styrene) for diverse applications, including: drilling fluids, paints, lube oil additives, adhesives, coatings, cosmetics, textile finishes, synthetic fibers, protective colloids, etc.[67-69]

Hydrogels based on crosslinked copolymers of vinyl pyrrolidone and 2-hydroxyethyl methacrylate are used in soft contact lenses.[70]

Vinyl pyrrolidone is also reportedly used as an intermediate for the production of modified phenolic resins used as plasticizers, dye intermediates, and textile assistants.[67]

There do not appear to be any likely substitutes in the primary uses of vinyl pyrrolidone as a monomer. Although substitutes exist for the use of vinyl pyrrolidone homopolymer and copolymers in end-use applications, due to the wide variety of these applications, a substantive discussion of such products is not possible.

The projected growth rate for the production of vinyl pyrrolidone is estimated at about 6-7% per year.

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16. ABSTRACT

This report describes the work carried out on Research Request No. 2 as specified by the Project Officer.

Market forecasts were prepared for 12 chemicals specified by the Project Officer and include a discussion of economic information for each chemical:

1,5-bis(chlorendo)cyclooctane, bis(2-chloroethyl) ether, bromoform, 2-chloroethanol, diethyl N,N-bis(2-hydroxyethyl)aminophosphonate, N-1,3-dimethylbutyl-N-phenyl-p-phenylenediamine, 4-methyl-7-diethylamino-coumarin, sodium fluoride, sodium fluorosilicate, stannous chloride, vinyl pyridine, and vinyl pyrrolidone.

The information presented includes the following: production and trade statistics; a discussion of current uses, and in some cases, past uses; possible substitute products for the chemical in specific applications, and the current price of those substitutes; trends in production levels (i.e., future growth rates); and factors affecting growth in the market for the chemical.

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