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# NIOSH

# Current Intelligence Bulletin 29

**OCTOBER 12, 1978** 

GLYCIDYL ETHERS

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U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

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The NIOSH Current Intelligence Bulletin is the primary product of the Current Intelligence System. The purpose of the Current Intelligence System is to promptly review, evaluate, and supplement new information received by NIOSH on occupational hazards that are either unrecognized or are greater than generally known.

As warranted by this evaluation, the information is capsulized and disseminated to NIOSH staff, other government agencies, and the occupational health community, including labor, industry, academia, and public interest groups. With respect to currently known hazard information this system also serves to advise appropriate members of the above groups of recently acquired specific knowledge which may have an impact on their programs or perception of the hazard. Above all, the Current Intelligence System is designed to protect the health of American workers and to allow them to work in the safest possible environment.

# ETHERS ARE TABULATED IN THE REAR PORTION OF THIS BULLETIN

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

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#### CURRENT INTELLIGENCE BULLETIN

#### GLYCIDYL ETHERS

October 12, 1978

The National Institute for Occupational Safety and Health (NIOSH) would like to inform the occupational health community of the possibility of adverse effects to the testes and the hemopoietic (blood forming) system in workers exposed to glycidyl ethers.

During development of a NIOSH criteria document on alycidyl ethers, a pattern of research findings emerged which indicates that some of the glycidyl ethers may be capable of producing testicular atrophy and hemopoietic abnormalities in various species of laboratory animals. Additionally, after the issuance of the June 1978 NIOSH criteria document, a 1957 study was released to NIOSH reporting testicular atrophy in laboratory rats exposed to n-butyl glycidyl ether. While none of the individual research reports are conclusive with respect to the ability of alycidyl ethers to produce permanent changes to the testes or hemopoietic system in laboratory animals, some of the changes observed may act as predisposing factors to systemic problems. SNIOSH is not aware of any studies investigating the possiblity of occurrence of testicular atrophy or hemopoietic abnormalities occurring in humans exposed to glycidyl ethers. The possibility of these effects occurring in humans is reason for concern. Therefore, NIOSH requests that any information regarding testicular atrophy or hemopoietic abnormalities observed in workers exposed to glycidyl ethers be reported to the NIOSH Division of Surveillance, Hazard Evaluations, and Field Studies, Industry-Wide Studies Branch, Medical Section, Telephone: (513) 684-3593.

NIOSH advises strict adherence to the detailed recommended occupational standard described in the glycidyl ethers criteria document. Particular attention should be given to appropriate medical surveillance in order to detect testicular atrophy or hemopoietic abnormalities in exposed workers. NIOSH requests that producers, distributors, users, professional associations, and unions transmit this information to their customers, employees, associates and members.

#### BACKGROUND

Glycidyl ethers are synthetic compounds characterized by the -C-O-CH<sub>2</sub>-CH-CH<sub>2</sub> group and find their major use as components of epoxy resin systems. The "diglycidyl ether of bisphenol A" has been a traditional basic active ingredient of

epoxy resins; other glycidyl ethers are frequently incorporated into epoxy resin systems as reactive diluents. The epoxy group of the glycidyl ethers reacts during the curing process and glycidyl ethers are therefore generally no longer present in completely cured products. Epoxy resins containing glycidyl ethers are used in a variety of applications including protective coatings, reinforced plastics, as well as bonding materials and adhesives.

Much occupational exposure to glycidyl ethers results from the use of proprietary or trade name products which do not disclose the presence of toxic agents in their formulations. This complicates efforts to take appropriate precautionary measures for the prevention of occupational disease. For example, unrecognized hazardous situations can occur where protective coatings containing epoxy resins are sprayed, thereby facilitating the inhalation of even non-volatile materials, and where there is skin contact with epoxy resins containing glycidyl ethers.

Data collected by the NIOSH National Occupational Hazards Survey (NOHS) have been used to estimate the number of people having potential occupational exposure to glycidyl ethers, as well as in identifying the industries in which the exposures occur. Pertinent data from NOHS are presented in Tables 1 and 2. NIOSH has previously estimated that approximately 1,000,000 workers are exposed to epoxy resins (1).

Table 1. NIOSH National Occupational Hazard Survey Estimates of Occupational Exposure to Glycidyl Ethers

Glycidyl Ether	Estimated Number of Workers Potentially Exposed*
Glycidyl Ethers**	71,000
Diglycidyl Ether of Bisphenol A	36,000
n-Butyl Glycidyl Ether	13,000
Phenyl Glycidyl Ether	8,000
Resorcinol Diglycidyl Ether	3,000
Allyl Glycidyl Ether	2,000
Octyl-Decyl Glycidyl Ether	200
Diglycidyl Ether	150
Isopropyl Glycidyl Ether	100
Triglycidyl Glycerol Ether	70

<sup>\*</sup>A worker may be exposed to more than one glycidyl ether, thus the exposure estimates are not additive. Due to the difficulty of obtaining data regarding the composition of trade name products, these estimates may be low.

<sup>\*\*</sup>Exposures were entered into the NOHS data base either under the specific glycidyl ether (when the information was available) or under the general term "glycidyl ethers" (when more specific information was not available). To the extent that an exposure to a specific glycidyl ether was reported as exposure to "glycidyl ethers," the data may underestimate occupational exposure to individual glycidyl ethers.

Table 2. Industries Where the Majority of Occupational Exposures to Glycidyl Ethers Occur\*

Transportation Equipment
Instruments and Related Products
Chemicals and Allied Products
Electrical Equipment and Supplies
Special Trade Contractors
Automotive Dealers and Service Stations
Transportation by Air
Miscellaneous Repair Services
Machinery, except electrical

Stone, Clay, and Glass Products
Medical and Other Health Services
Fabricated Metal Products
Building Materials and Farm Equipment
Food and Kindred Products
Rubber and Plastic Products
Furniture and Fixtures
Amusement and Recreation Services
Leather and Leather Products

Communication

The National Occupational Hazard Survey, conducted between 1972 and 1974, was based on a sample of businesses selected by the Bureau of Labor Statistics and consisted of approximately 5,000 establishments employing nearly 900,000 workers in 67 standard metropolitan areas throughout the United States. This sample was representative of non-agricultural businesses covered under the Occupational Safety and Health Act of 1970.

NIOSH is not aware of any studies investigating the possible occurrence of testicular atrophy or hemopoietic abnormalities in humans exposed to glycidyl ethers. However, other effects observed in humans include dermatitis, irritation, and allergic reactions. The NIOSH glycidyl ethers criteria document (1) provides a detailed evaluative review of reported adverse effects resulting from exposure to glycidyl ethers.

# LABORATORY ANIMALS -- Testicular Atrophy and Hemopoietic Abnormalities

Studies in several different research laboratories indicate that some of the glycidyl ethers are capable of producing adverse effects to the testes and hemopoietic system in various species of laboratory animals. Reported testicular abnormalities (including testicular atrophy with decreased spermatogenic activity) following exposure to glycidyl ethers are presented in Table 3. Table 4 summarizes reported hemopoietic abnormalities following exposure to glycidyl ethers, including alteration of the leukocyte count, atrophy of lymphoid tissue, and bone marrow cytotoxicity. These abnormalities were usually observed along with pneumonia and/or toxemia, and therefore may be secondary effects. However, especially in light of the generalized reduction in leukocytes and the atrophy of lymphoid tissues, the observed hemopoietic abnormalities may have been predisposing factors to pneumonia. While none of the individual research reports are conclusive with respect to the ability of glycidyl ethers to produce permanent changes to the testes or hemopoietic system in laboratory animals, the pattern of effects displayed in Tables 3 and 4 is reason for concern.

The NIOSH glycidyl ethers criteria document (1) contains an evaluative review of the literature on effects of exposure to glycidyl ethers. Reported adverse effects in laboratory animals include sensitization, and skin and eye irritation, as well as mutagenic and tumorigenic activity.

<sup>\*</sup>These are standard industrial titles from the <u>Standard Industrial Classification</u>
<u>Manual</u> (2).

Table 3. Reported Testicular Disorders Following Exposure to Glycidyl Ethers

Agent (reference)	Animal	Exposure	Reported Testicular Disorder
Allyl Glycidyl Ether (3)	Rat	400 mg/kg intramuscular injections on days 1,2,8, and 9 animals sacrificed on day 12	focal necrosis of the testis in 1 of 2 of the 3 surviving rats
n-Butyl Glycidyl Ether (4)	Rat	38 ppm, 75 ppm, 150 ppm, 300 ppm by inhalation, seven hours/day, five days/week for a total of 50 exposures	atrophic testes in 5 of 10 at 300 ppm; very small testes in 1 of 10 at 300 ppm; slight patchy atrophy of the testes in 1 of 10 animals at 75 ppm
Diglycidyl Ether (5)	Rat	125 mg/kg, 250 mg/kg cutaneous daily appli- cation, 5 days/week, total of six applications	focal necrosis of the testes
		3 ppm by inhalation 4 hours/day, 5 days/week total of 19 exposures	necrosis of the tubules of the testes in 1 of 15 animals
		0.3 ppm by inhalation, 4 hours/day, 5 days/week total of 60 exposures	poorly defined focal degeneration of the germinal epithelium in 5 of 10 animals
	Rabbit	single 24 hour inhalation exposure of 24 ppm	greatly atrophied testes in two animals which died on the evening of the fifth day
Phenyl Glycidyl Ether (6)	Rat	1.75 ppm, 5.84 ppm, 11.20 ppm by inhalation 6 hours/day for 19 consecutive days	Initial Report: focal degenerative changes involving the seminiferous tubules in both gonads in 1 of 8 at 1.75 ppm, 1 of 8 at 5.84 ppm, and 3 of 8 11.20 ppm
			Supplemental Examination:  1 of 8 in each of 1.75, 5.84, and 11.20 ppm groups had a marked degree of gonad change
Triethylene Glycol Diglycidyl Ether (7)	Mouse	7208 mg/kg total dose administered in 12 intraperitoneal injection, 3 per week for four weeks, animals sacrificed 39 weeks after the first injection	testular atrophy with decreased spermatogenic activity

Table 4. Reported Hemopoietic Abnormalities in Animals Following Exposure to Glycidyl Ethers

Agent (reference)	Animal	Exposure	Reported Abnormality
injections of and 9 animals sac		400 mg/kg intramuscular injections on days 1,2,8, and 9 animals sacrificed on day 12	atrophy or loss of lymphoid tissue in 2 of 3 rats decreased leukocyte count
<u>n</u> -Butyl Glycidyl Ether (3)	Rat	400 mg/kg intramuscular injections for 3 consecutive days	increased leukocyte count
Butanediol Diglycidyl Ether (8)	Rat	100 mg/kg, 200 mg/kg single intraperitoneal injection	bone marrow cytotoxicity
Diethylene Glycol Diglycidyl Ether (8)	Rat	100 mg/kg, 200 mg/kg, 400 mg/kg single intraperitoneal injection	bone marrow cytotoxicity
Diglycidyl Ether (5)	Rat	single application of 0.5 g/kg, 1 g/kg to shaved backs	decreased leukocyte count
		daily skin application of 125 mg/kg, 5 days/week for 4 weeks; skin application on days 1,2,3,4,5, and 8 of 250 mg/kg, 500 mg/kg	decreased leukocyte count increase in percentage of polymorphonuclear cells
			fewer nucleated cells of the bone marrow
			enlarged myeloid cells in 250 and 500 mg/kg groups.
			lymphoid atrophy of the thymus at 500 mg/kg.
		3 ppm by inhalation, 4 hours/day, 5 days/week, total of 19 exposures	decreased leukocyte count
	Rabbit	Single application of 1.13 g/kg to shaved back	decreased leukocyte count
		Single intravenous injection of 50 mg/kg, 100 mg/kg,	decreased leukocyte count
		200 mg/kg	23 nucleated erythrocyte per 100 leukocytes in 100 mg/kg group
	Dog	25 mg/kg intravenous injection, 2 injections, six days apart, in two dogs 3 weekly injections in one dog	decreased leukocyte count
Phenyl Glycidyl Ether (3)	Rat	400 mg/kg intramuscular injections for 3 consecutive days	increased leukocyte count

## NIOSH RECOMMENDATION

Reports from different laboratories present a pattern of findings indicating that some of the glycidyl ethers may be capable of producing testicular atrophy and hemopoietic abnormalities in various species of laboratory animals. While none of the individual research reports are conclusive with respect to the ability of glycidyl ethers to produce permanent changes to the testes or hemopoietic system in laboratory animals, some of the changes observed may act as predisposing factors to systemic problems. NIOSH is not aware of any studies investigating the possible occurrence of testicular atrophy or hemopoietic abnormalities in humans exposed to glycidyl ethers. The possibility of these effects occurring in humans is reason for concern. Therefore, the occupational health community is advised of the possibility of these effects appearing in workers exposed to glycidyl ethers.

The "NIOSH Criteria for a Recommended Standard . . . Occupational Exposure to Glycidyl Ethers" was transmitted to the Occupational Safety and Health Administration (OSHA), Department of Labor, on June 30, 1978 (1). This criteria document contains detailed recommendations regarding maximum exposure levels, medical surveillance, labeling and posting, personal protective clothing and equipment, informing employees of hazards, work practices, sanitation, monitoring, and recordkeeping requirements as well as sampling and analytical procedures. Existing occupational exposure limits for specific glycidyl ethers are listed in Table 5.

Table 5. Existing Occupational Exposure Limits for Specific Glycidyl Ethers

	Present OSHA Exposure Standard (9)			NIOSH Recommended Exposure Standard (1) (Ceiling)				
Allyl Glycidyl Ether n-Butyl Glycidyl Ether Diglycidyl Ether Isopropyl Glycidyl Ether Phenyl Glycidyl Ether	10 50 0.5 50 10	bbm bbm bbm bbm	(45 (270 (2.8 (240 (60	mg/cu m) * mg/cu m) ** mg/cu m) ** mg/cu m) ** mg/cu m) **	45 30 1 240 5	mg/cu m mg/cu m mg/cu m mg/cu m	(9.6 (5.6 (0.2 (50	ppm) ppm) ppm) ppm)

<sup>\*</sup>Ceiling

<sup>\*\*8-</sup>hour time-weighted average

NIOSH advises strict adherence to this detailed recommended occupational standard for glycidyl ethers described in the NIOSH criteria document. Particular attention should be given to appropriate medical surveillance in order to detect testicular atrophy or hemopoietic abnormalities in exposed workers.

NIOSH requests that any information regarding testicular atrophy or hemopoietic abnormalities in workers exposed to glycidyl ethers be reported to the NIOSH Division of Surveillance, Hazard Evaluations, and Field Studies, Industry-Wide Studies Branch, Medical Section, Telephone: (513) 684-3593.

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**Acting Director** 

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# IDENTIFIERS AND SYNONYMS FOR ALLYL GLYCIDYL ETHER

Chemical Abstracts Service Registry Number 106-92-3 NIOSH RTECS Number RR0875000 Chemical Formula C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>

AGE

Allyl 2,3-Epoxypropyl Ether

Allyl Glycidyl Ether

1-Allyloxy-2,3-epoxypropane

1,2-Epoxy-3-allyoxypropane

Ether, Allyl 2,3-epoxypropyl

Glycidyl Allyl Ether

Oxirane, [(2-Propenyloxy)methyl]-Propane, 1-(Allyloxy)-2,3-epoxy-

# · IDENTIFIERS AND SYNONYMS FOR p-BUTYL GLYCIDYL ETHER

Chemical Abstracts Service Registry Number 2426-08-6 NIOSH RTECS Number TX4200000 Chemical Formula C<sub>7</sub>H<sub>14</sub>O<sub>2</sub>

BGE

ERL 0810

1-Butoxy-2,3-epoxypropane 3-Butoxy-1,2-epoxypropane Butyl Glycidyl Ether n-Butyl Glycidyl Ether 2,3-Epoxypropyl Butyl Ether

Ether, Butyl 2,3-Epoxypropyl Ether, Butyl Glycidyl Glycidyl Butyl Ether Oxirane, (Butoxymethyl)-

Propane, 1-Butoxy-2,3-epoxy-

# IDENTIFIERS AND SYNONYMS FOR DIGLYCIDYL ETHER

Chemical Abstracts Service Registry Number 2238-07-5 NIOSH RTECS Number KN2350000 Chemical Formula C6H10O3

Bis(2,3-Epoxypropyl) Ether

DGE

Di(2,3-epoxy)propyl Ether

Diglycidyl Ether

Ether, Bis(2,3-epoxypropyl)

Ether, Diglycidyl Glycidyl Ether

NSC 54739

Oxirane, 2,2'- [Oxybis(methylene)]bis-

# IDENTIFIERS AND SYNONYMS FOR DIGLYCIDYL ETHER OF BISPHENOL A

Chemical Abstracts Service Registry Number 1675-54-3 NIOSH RTECS Number TX3800000 Chemical Formula C<sub>21</sub>H<sub>24</sub>O<sub>4</sub>

4,4'-Bis(2,3-epoxypropoxy)diphenyldimethylmethane

2,2-Bis [p-(2,3-epoxypropoxy)phenyl]propane

2,2-Bis #-(2,3-epoxypropoxy)phenyl]propane

Bis(4-glycidyloxyphenyl)dimethylmethane

2,2-Bis(p-glycidyloxyphenyl)propane

2,2-Bis(4-glycidyloxyphenyl)propane

Bis(4-hydroxyphenyl)dimethylmethane Diglycidyl Ether

2,2-Bis(p-hydroxyphenyl)propane Diglycidyl Ether

2,2-Bis(4-hydroxyphenyl)propane Diglycidyl Ether

Bisphenol A Diglycidyl Ether

D.E.R. 332

Dian Diglycidyl Ether

Diglycidyl Bisphenol A

Diglycidyl Bisphenol A Ether

Diglycidyl Diphenylolpropane Ether

Diglycidyl Ether of 2,2-Bis(p-hydroxyphenyl)propane

Diglycidyl Ether of 2,2-Bis(4-hydroxyphenyl)propane

Diglycidyl Ether of Bisphenol A

Diglycidyl Ether of 4,4'-Isopropylidenediphenol

4,4'-Dihydroxydiphenyldimethylmethane Diglycidyl Ether

p,p'-Dihydroxydiphenyldimethylmethane Diglycidyl Ether

Diomethane Diglycidyl Ether

EPI-REZ 510

Epoxide A

ERL-2774

4,4'-Isopropylidenebis[1-(2,3-epoxypropoxy)benzene]

4,4'-Isopropylidenediphenol Diglycidyl Ether

2,2' [(1-Methylethylidene)bis(4,1-phenyleneoxymethylene)] bisoxirane Oxirane, 2,2' [(1-Methylethylidene)bis(4,1-phenyleneoxymethylene)] bis-

Propane, 2,2-Bis [(p-(2,3-epoxypropoxy)phenyl]-

# IDENTIFIERS AND SYNONYMS FOR ISOPROPYL GLYCIDYL ETHER

Chemical Abstracts Service Registry Number 4016-14-2 NIOSH RTECS Number TZ3500000 Chemical Formula C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>

1,2-Epoxy-3-isopropoxypropane Glycidyl Isopropyl Ether **IGE** 

3-Isopropoxy-1,2-epoxypropane (Isopropoxymethyl)oxirane

Isopropyl Glycidyl Ether [(1-Methylethoxy)methyl] oxirane Oxirane, [[1-Methylethoxy] methyl]-Propane, 1,2-Epoxy-3-isopropoxy-

## DENTIFIERS AND SYNONYMS FOR PHENYL GLYCIDYL ETHER

Chemical Abstracts Service Registry Number 122-60-1 NIOSH RTECS Number TZ3675000 Chemical Formula C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>

Benzene, (2,3-Epoxypropoxy)1,2-Epoxy-3-phenoxypropane
2,3-Epoxypropyl Phenyl Ether
2,3-Epoxypropylphenyl Ether
Ether, 2,3-Epoxypropyl Phenyl
Glycidol Phenyl Ether
Glycidyl Phenyl Ether
Oxirane, (Phenoxymethyl)PGE
Phenol Glycidyl Ether
1-Phenoxy-2,3-epoxypropane
3-Phenoxy-1,2-epoxypropane

3-Phenoxy-1,2-propylene Oxide (Phenoxymethyl)oxirane Phenoxypropene Oxide Phenoxypropylene Oxide γ-Phenoxypropylene Oxide Phenyl 2,3-Epoxypropyl Ether Phenyl Glycidyl Ether Phenylglycidyl Ether 3-Phenyloxy-1,2-epoxypropane Propane, 1,2-Epoxy-3-phenoxy-

## IDENTIFIERS AND SYNONYMS FOR RESORCINOL DIGLYCIDYL ETHER

Chemical Abstracts Service Registry Number 101-90-6 NIOSH RTECS Number VH1050000 Chemical Formula  $\rm C_{12}H_{14}O_4$ 

Araldite ERE 1359
Benzene, m-Bis(2,3-epoxypropoxy)Diglycidyl Resorcinol Ether
m-Bis(2,3-epoxypropoxy)benzene
1,3-Bis(2,3-epoxypropoxy)benzene
NCI - C54966
Oxirane, 2,2'- [1,3-Phenylenebis(oxymethylene]] bis2,2- [1,3-Phenylenebis(oxymethylene)]bisoxirane
RDGE
Resorcinol Bis(2,3-epoxypropyl) Ether
Resorcinol Diglycidyl Ether
Resorcinol Glycidyl Ether
Resorcinyl Diglycidyl Ether

# CHEMICAL STRUCTURES OF SOME GLYCIDYL ETHERS

# CUMULATIVE LIST OF NIOSH CURRENT INTELLIGENCE BULLETINS

*	1. 2.	Chloroprene Trichloroethylene (TCE)	- January 20, 1975 - June 6, 1975
*	3.	Ethylene Dibromide (EDB)	- July 7, 1975
*	4.	Chrome Pigments	- June 24, 1975
			- October 7, 1975
		·	- October 8, 1976
*	5.	Asbestos	- August 8, 1975
*	6.	Hexamethylphosphoric Triamide (HMPA)	- October 24, 1975
*	7.	Polychlorinated Biphenyls (PCBs)	- November 3, 1975
		•	- August 20, 1976
	8.	4,4'-Diaminodiphenylmethane (DDM)	- January 30, 1976
*	9.	Chloroform	- March 15, 1976
	10.	Radon Daughters	- May 11, 1976
	11.	Dimethylcarbamoyl Chloride (DMCC)	
		Revised	- July 7, 1976
	12.	Diethylcarbamoyl Chloride (DECC)	- July 7, 1976
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	14.	Inorganic Arsenic - Respiratory	
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*	15.	Nitrosamines in Cutting Fluids	- October 6, 1976
*	16.	Metabolic Precursors of a Known	
		Human Carcinogen, Beta-Naphthylamine	- December 17, 1976
*	17.	2-Nitropropane	- April 25, 1977
*	18.	Acrylonitrile	- July 1, 1977
	19.	2,4-Diaminoanisole in Hair and Fur Dyes	- January 13, 1978
*	20.	Tetrachloroethylene (Perchloroethylene)	- January 20, 1978
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		Direct Brown 95 Benzidine Derived Dyes	- April 17, 1978
*	25.	Ethylene Dichloride (1,2-Dichloroethane)	- April 19, 1978
	26.	NIAXº Catalyst ESN	- May 22, 1978
	27.	Chloroethanes - Review of Toxicity	- August 21, 1978
*	28.	Vinyl Halides - Carcinogenicity	- September 21, 1978
	29.	Glycidyl Ethers	- October 12, 1978

NOTE: Bulletins #1 through #18 have been reprinted as a NIOSH publication, #78-127, for the convenience of those that desire a complete series of Current Intelligence Bulletins. Distribution of this publication and single copies of Bulletins #19 and later are available from NIOSH Publications Dissemination, Division of Technical Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

<sup>\*</sup>Cancer related bulletins

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