Survey for N-nitroso Compounds
at
Vulcan Steel Foundry
Oakland, CA

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Place Visited	Vulcan Steel Foundry Oakland, CA
Date of Visit	October 1, 1980
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SIC Code	3321
Purpose of Visit	To determine whether N-nitroso compounds are present or formed in foundries during the manufacturing of steel and iron castings

Introduction

N-nitroso compounds (nitrosamines) have the general formula R_1R_2N-NO, with R_1 and R_2 being virtually any organic group. These compounds are usually formed by the reaction of a secondary amine with nitrite in an acid solution (1, 2), however these are not the only conditions that can give rise to these compounds. It has been demonstrated that N-nitroso compounds can be produced in: organic solvents (3), alkaline solutions (4), gas phase reactions (5), and on surface via airborne oxides of nitrogen (6, 7). Tertiary amines have also been shown to form N-nitroso compounds (8). The nitrosyl radical (-NO) can be derived from oxides of nitrogen (X-NO, NO_2, N_2O_3 or N_2O_4) (4, 5, 6, 7), organic and inorganic nitrite or via trans-nitrosation by other N-nitroso compounds (9). It has also been shown that these reactions can be increased by catalysts such as formaldehyde or chloral (10), or metal ions (11) and that they can be inhibited by α-tocopherol (12), ascorbate (13), and sulfamic acid (14). In short, these compounds can be produced in almost any situation where the precursors co-exist.

Interest in the possible human health hazard that N-nitroso compounds may pose began following the observation in animal studies of the toxic and carcinogenic effects of N-nitrosodimethylamine (NDMA) (15). The toxic effect of NDMA on humans was first reported by Freud in 1937 (16) who described its hepatotoxic effects on two chemists that had been accidentally poisoned by this compound. Since these first findings, N-nitroso compounds have been studied extensively in experiments with laboratory animals. More than 100 of the 130 different compounds tested have been shown to be carcinogenic (15, 17, 18, 19). N-nitrosodiethylamine (NDEA), for example, has been tested in the rat, African white-tailed rat, mouse, S.G. hamster, Chinese hamster, European hamster, guinea pig, rabbit, dog, pi , trout, parakeet and monkey, and has been shown to be carcinogenic in all these species.

The site where the tumor developed depended upon the chemical structure of the N-nitroso compound, the animal being tested and on the route of administration. N-nitroso compounds have been shown to affect the bladder, bronchi, central nervous system, earduct, esophagus, eyelid, duodenum, forestomach, glandular stomach, hematopoietic system, intestine, jaw, kidney, larynx, lung, nasal cavity, oral cavity, ovary, liver, mammary glands, pancreas, pelvis, peripheral nervous system, pharynx, respiratory tract, skin, testis, tongue, trachea, uterus and vagina (18).

Three N-nitrosamines that were tested in dose response studies with rats were shown to be extraordinarily potent carcinogens. The apparent 'no effect level' at which no statistical difference between the test animals and the controls could be observed, was found to correspond to dietary levels of 1000 μg/kg (1 ppm) of N-nitrosodimethylamine (20), 1000 μg/kg (1 ppm) of N-nitrosodiethylamine (21), and 5000 μg/kg (5 ppm) of N-nitrosopyrrolidine (22). Thus, in a rat population of under 100 animals, between 1 and 5 ppm of these nitrosamines in the diet were marginally carcinogenic.

The comparative in vitro metabolism of N-nitrosodimethylamine is similar in both the human and rat liver (23). Furthermore, the rate of metabolism in human liver slices is comparable to that in the rat liver, with the levels of nucleic acid methylation being similar to the two species (24). In acute toxicity experiments with high doses, nitrosamines generally produce centrilobular necrosis in most animal species.

While many of these compounds have been demonstrated to be potent animal carcinogens, their carcinogenic risk to man (the probability that defined exposure to these chemicals will lead to cancer) has not yet been determined. In order to assess this risk it is first necessary to locate sufficient populations of exposed people.

Until as recently as 1975 the primary interest in human exposure to these carcinogenic compounds centered around their occurrence in nitrite preserved foods, cheese products, fish and fish meal, biological samples, tobacco, alcoholic beverages and in vivo formation from precursor chemicals. With the finding of NDMA in the atmospheres near manufacturing facilities producing and/or using dimethylamine (25, 26, 27) the emphasis on human exposure to these compounds began to shift to the workplace where, it has been speculated, human exposure to these compounds may be the highest (25).

Further discoveries of N-nitroso compounds in cosmetics (28), tobacco smoke (29), indoor atmosphere under conditions of excessive tobacco smoking (30), in synthetic cutting fluids (31), and in some widely used herbicides (32), have further shifted the emphasis of the environmental search for human exposure to these compounds. It is now apparent that any situation where the precursor of these compounds (amines and nitrosating agents) may exist together, that there is a high likelihood of finding N-nitroso compounds.

Many secondary amines such as dimethylamine, diethylamine and morpholine are produced in large quantities for both industrial and consumer use. Products manufactured from these amines are used in agricultural chemicals, detergents, rust inhibitors, rubber additives, solvents, drugs, plastics, leather tanning, textiles, cosmetics and in synthetic cutting and grinding fluids (33). Given the widespread use of secondary amines and the ever present nitrogen oxides of an industrial society, the likelihood of N-nitrosamines being formed in some products or in an industrial situation where these compounds may occur together, is high.

Until this study the human population groups that were identified as being potentially exposed to large amounts of carcinogenic N-nitroso compounds included; chemical workers at a factory making unsymmetrical dimethylhydrazine from N-nitrosodimethylamine (26, 34), agricultural workers handling pesticides contaminated with nitrosamines (32), machinists using synthetic cutting and grinding fluids contaminated with N-nitrosodiethanolamine (31), and persons using facial cosmetics contaminated with N-nitrosodiethanolamine (28). During this present study two other groups: rubber workers exposed to N-nitrosomorpholine (35) and leather tanners exposed to

N-nitrosodimethylamine in tannery air, (36) have also been discovered.

The knowledge that man may be exposing himself to relatively large quantities of N-nitroso compounds is a recent development which may have important implications in carcinogenesis. If N-nitroso compounds are a cause of cancer in man, then minimizing exposure to these compounds could be a significant milestone in cancer prevention. But direct evidence for the carcinogenicity of N-nitroso compounds in man is lacking. There is, however, a substantial amount of circumstantial evidence which makes it unlikely that man alone will be resistant to their carcinogenic assault. Recent advances in epidemiology, plus improved technology in the analytical chemistry of N-nitroso compounds, coupled with a better understanding of the formation chemistry of N-nitroso compounds, makes it possible to begin the quest for direct evidence relating N-nitroso compounds to possible cancer in man.

Until epidemiological assessments can be made it must be assumed, on the basis of many animals studies, that man will not be uniquely resistant to the carcinogenic action of nitrosamines. Indeed if human populations are found to have excessive (higher than justifiable) exposure to these compounds, prompt action should be taken to eliminate or reduce their exposure. Since cancer produced from carcinogenic compounds is a delayed toxic effect, and since animal studies show dose related responses to these agents, it would be prudent to assume (until evidence can be obtained) that any exposure to the carcinogenic N-nitrosamines constitute a risk. This study by the National Institute for Occupational Safety and Health (NIOSH) is the first attempt to determine worker's exposure to N-nitroso compounds in a variety of industrial facilities. It assesses not only the extent of worker exposure to these agents, but also how they are exposed and how best to eliminate or reduce their risk.

Iron and Steel Casting Industry

Metal castings are produced by pouring the molten metal into refractory molds where it solidifies into the desired shape and contour. This industry has been in existence since about 1845 when the first steel castings were made using sand molds to produce horseshoes, and molds made from loam to produce steel church bells (Steel Casting Handbook, 4th Edition - Steel Founders Society of America). There are now approximately three hundred foundries in the United States. These plants range in size, according to production, from 10 to 100 tons per month to those which are capable of producing several thousand tons a month. Each foundry is an individual entity which can be highly specialized or easily adaptable to the production of a wide variety of castings. While all of these foundries may differ in product line or specific methods, they all use molds and molten metal to produce the desired casting.

The refractory material most widely used to make molds and cores (cores are used to exclude metal from areas of the final casting) is silica sand. The molds are fabricated using patterns to imprint the desired shape of the casting and binders to hold the sand in shape.

Some of the sand binding materials include the following: sodium bentonite, cereals, water, clay, phenol formaldehyde, resins, isocyanates, oils, amine catalyzed resin systems, etc. Interest in surveying this industry for the presence of N-nitroso compounds centers around the sand core fabrication process that utilizes amines as a part of the sand binding system. These cores are made by injecting sand, containing binding agents, into molds followed by the injection of an amine catalyst. This interest stems from an OSHA report of November 15, 1978 stating that N-nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA) were found in the atmosphere of a foundry. The reported levels of NDMA were from 0.1 - 0.8 $\mu g/m^3$ and from 0.1 to 1.4 $\mu g/m^3$ for NDEA. These nitrosamines were found in air samples collected in the sand core production area where amines were being used. The amine being used by this foundry was reported to be triethylamine (TEA)

Other amines that could be used in this sand core process includes dimethylamine (DMA), trimethylamine (TMA), N-ethyldimethylamine (EDA), and diethylamine DEA. Some of these amines could be present as contaminants in the specific amine being used or they could be produced when hot metal is poured into molds made with amines. In any event, these amines could serve as nitrosamine precursors. Compounds such as dimethylamine and diethylamine (secondary amines) have been demonstrated to form their corresponding nitrosamines from atmospheric oxides of nitrogen. Tertiary amines such as N-ethyldimethylamine and triethylamine are,on the other hand less likely to form nitrosamines under the same conditions. As for the oxides of nitrogen, these can be produced by combustion processes and by air contacting hot metal.

Plant Description

The Vulcan Steel Foundry manufactures carbon, alloy and stainless steel castings. The plant was built during 1920 and presently has four separate buildings occupying about three acres. The largest of these buildings has about 100,000 square feet and is the main production area. The plant employs about 155 with 11 in management producing 300-350 tons of castings per month. The molding and core production facilities are located in separate areas within the main production area. This plant does not use amines in its core making production but it does make hot shell cores and no bake isocure cores. The plant produces large castings (pumps and valves for the oil industry) using green sand moldings.

Experimental

Plant Survey Protocol

After a brief plant tour, five sample sites were selected for area air sampling for both N-nitroso compounds and precursor amines. The areas selected were the core making room, the no bake core production, the green sand mold room, the mold pouring area and the sand shake out area. These areas were selected because they represented a cross section of this foundry's general activities. Two battery operated MSA Model C pumps, one equipped with a ThermoSorb/N air sampling cartridge for trapping N-nitroso compounds, and the other with a ThermoSorb/A air sampling cartridge for trapping amines, were placed side-by-side at each sampling site. These pumps were then operated for three hours with air sampling rates of from 1.5 L/min to 2.0 L/min.

Since amines were not used in this plant the site selections were chosen to represent the general atmosphere within the plant. During our initial plant tour we did not observe any potential sources of either amines or of N-nitroso compounds. We did, however, observe several combustion processes which could contribute oxides of nitrogen to the plant's atmosphere.

The object of collecting air samples for amines was to determine if the atmosphere in the sampled areas contained any amines which could give rise to N-nitroso compounds. Typically the amines that could give rise to these compounds would be secondary amines such as dimethylamine, diethylamine, morpholine, etc.

We also collected a composite sand sample from the waste sand within the core manufacturing area. This sample was collected to determine if amines were present in the sand-binder mix.

Results

No N-nitroso compounds or amines were found in this plant's atmosphere (Tables I, II). These findings were not unexpected since the plant did not use the amine sand core production process. We also failed to find any amines in the composite sand sample.

Table I

NITROSAMINE Results - Air Samples

Vulcan Steel Foundry

Oakland, CA

Sample #	Collection Method	Sample Location	N-nitroso Compound Detected
16164	ThermoSorb/N	Core Making Room	ND*
16166	ThermoSorb/N	No Bake Core Production	ND
16168	ThermoSorb/N	Mold Room	ND
16170	ThermoSorb/N	Sand Shake Out Area	ND
16172	ThermoSorb/N	Mold Pouring Area	ND

* ND - None detected, detection limit = 0.1 $\mu g/m^3$ for N-nitrosodimethylamine

Table II

Amine Results - Air Samples
Vulcan Steel Foundry
Oakland, CA

Sample #	Collection Method	Sample Location	Amine Detected* DMA	TMA	DEA	TEA
16165	ThermoSorb/A	Core Room	ND**	ND	ND	ND
16167	ThermoSorb/A	No Bake Core Production	ND	ND	ND	ND
16169	ThermoSorb/A	Mold Room	ND	ND	ND	ND
16171	ThermoSorb/A	Sand Shake Out Area	ND	ND	ND	ND
16173	ThermoSorb/A	Mold Pouring Area	ND	ND	ND	ND

* Amines Detected - DMA - Dimethylamine
TMA - Trimethylamine
DEA - Diethylamine
TEA - Triethylamine

** None Detected - detection limit 0.5 $\mu g/m^3$ for dimethylamine

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