

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH  
CINCINNATI, OHIO 45202

HEALTH HAZARD EVALUATION DETERMINATION  
REPORT NO. 72-88

N. L. INDUSTRIES, INC.  
TITANIUM PIGMENT DIVISION  
ST. LOUIS, MISSOURI 63111  
SEPTEMBER 1973

I. TOXICITY DETERMINATION

Based upon the results of the medical evaluation reported below, it has been determined that Monoisopropanolamine (MIPA) was toxic and represented a definite cutaneous hazard upon direct contact with the skin to those workmen failing to utilize proper protective clothing, gloves, and good work practices. Five instances of primary irritant contact dermatitis due to direct skin exposure to MIPA were identified. Most employees working with the substance recognized its irritant properties, but were not wearing appropriate protective clothing at the time of contact. Another individual also noted upper respiratory tract and eye irritation due to this substance. No new cases of irritation or dermatitis have appeared since the discontinuance of this substance. Proper protective measures should eliminate this problem if MIPA or Triethanolamine (TEA) is reintroduced into the workplace.

It is further determined that a toxic condition to workers from exposure to Titanium Dioxide ( $TiO_2$ ) dust does not exist at concentrations found in this work environment. This finding is based upon: (1) personal air sample results which were well below those levels reported to cause abnormal effects in exposed workers; and (2) the lack of pulmonary or other noncutaneous health problems identified during the course of this investigation.

In the interest of providing a more desirable working environment, general recommendations consistent with good industrial hygiene practices have been submitted to management concerning these potential hazards.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report of the evaluation are available upon request from the Hazard Evaluation Services Branch, NIOSH, U. S. Post Office Building, Room 508, Fifth and Walnut Streets, Cincinnati, Ohio 45202. Copies have been sent to:

- a) N. L. Industries, Inc., Titanium Pigment Division,  
St. Louis, Missouri
- b) Authorized Representative of Employees
- c) U.S. Department of Labor - Region VII
- d) NIOSH - Region VII

For the purposes of informing the approximately 70 "affected employees" the employer will promptly "post" the Determination Report in a prominent place(s) near where affected employees work for a period of 30 calendar days.

### III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized representative of employees to evaluate the potential hazards associated with the use of monoisopropanolamine (MIPA) and Titanium Dioxide ( $TiO_2$ ) in the milling department of N. L. Industries, Inc., Plant in St. Louis, Missouri. MIPA was replaced by triethanolamine (TEA) in early 1973; and TEA was eliminated from the process without substitution prior to our final site visit.

### IV. HEALTH HAZARD EVALUATION

#### A. Plant Process - Conditions of Use

This large plant produces titanium dioxide pigment from ilmenite ore and occupies an 80 acre site bordering the Mississippi River. Enriched ilmenite ore is digested by reacting it with sulfuric acid, steam, and water; producing  $TiO_2$  which is further purified (99% pure) by precipitation, bleaching, washing, filtering, and calcining at extremely high temperatures. The pigment is then ground to specification in large vertical Raymond Mills located in the area covered by this Determination Report. These Mills and ancillary equipment are housed in a five story building; the bottom floor contains nine operational 50" mills; the second floor contains bagging facilities and four operational 60" mills; the third floor contains storage bins; the fourth floor contains the fan room with bag filters;

and the fifth floor contains the platform and top of the "A" mill bin. Small quantities of MIPA (12-18 cc's per minute) were metered into the mills to reduce any caking tendency assuring that the product was ground to exact specification. Approximately 70 operators, cleanup, and maintenance employees were occasionally exposed to MIPA and  $TiO_2$  (semi-saturated with MIPA) during maintenance operations or when a leak occurred in the system. MIPA was replaced by TEA in early 1973, and TEA was discontinued without substitution prior to our final evaluation. Following particle sizing (submicron to several microns in size) for specific products, the  $TiO_2$  is bagged for sale or sent to the wet mill area for further processing. The 60" mills were not operational at the time of our initial visit. There are 4 shifts which operate 3 shifts a day for 7 days a week in the production areas. The main complaints were from the dusty conditions during operations, and more particularly from MIPA contact during maintenance operations.

#### B. Evaluation - General

A medical-environmental team visited the facility on October 19-20, 1972 and May 30-31, 1973 to assess potential problem areas and to complete the evaluation. Conditions were very dusty (airborne dust and dust on floor, rafters, etc.) from visual observations made at the time of the initial visit. Conditions were very much improved at the time of our final visit to the area covered by this request. Separate exit interviews were held with representatives of management and union at the completion of both visits to discuss preliminary findings.

### C. Evaluation Criteria

The following is a brief resume of the pathologic effects of substances alleged to be hazardous:

Monoisopropanolamine (MIPA) and its vapor are not considered to be toxic in the usual industrial setting. High concentrations may be irritating to the upper respiratory tract and eyes. Splashes directly into the eye may result in serious injury. It is known to be a moderate skin irritant and may cause dermatitis as the result of a single direct exposure. Prolonged contact may result in more severe irritation. It is not thought to be a cutaneous sensitizer, ie. allergenic. A study carried out by Mr. Vernon B. Perone, Toxicology Branch, Division of Laboratories and Criteria Development, NIOSH confirmed the inability of this substance and TEA to cause cutaneous sensitization. It was noted that aqueous concentrations exceeding 25% produced primary irritation when directly applied to intact animal skin. Concentrations exceeding 1% were found to be capable of irritating previously abraded skin.

Triethanolamine (TEA) has properties very similar to MIPA but is considered to be less toxic. TEA was studied in an identical manner and found to be irritating in aqueous concentrations exceeding 10% for intact skin and 1% for abraded skin. These substances are no longer used in the workplace.

Titanium Dioxide (TiO<sub>2</sub>). Titanium, its oxides, and salts are all regarded as being essentially innocuous. Titanium derivatives including the oxides have been used in treating various skin disorders and during World War II large amounts were used as a protective skin cream to prevent flash burns. Experience indicates that it is completely harmless when used as a constituent of cosmetic preparations. In man the hazard of lung fibrosis or "titanicosis" from chronic inhalation is regarded as very slight and no

definite cases have been reported. Numerous investigators have reported no abnormal clinical, radiological or pulmonary function test findings among long-term operatives exposed to titanium dust.

The Occupational Safety and Health Standards as promulgated by the U.S. Department of Labor (Title 29, Code of Federal Regulations, Chapter XVII, Part 1910.93, entitled "Air Contaminants" as published in the Federal Register on October 18, 1972) applicable to  $TiO_2$  on an 8-hour time-weighted average are as follows:

Inert or Nuisance Dust

Total Dust - 15 milligrams of dust per cubic meter of air -  $mg/M^3$

Respirable Dust - 5 milligrams of dust per cubic meter of air -  $mg/M^3$

Occupational health standards are established at levels designed to protect workers occupationally exposed to a substance on an 8-hours-per-day, 40-hours-per-week basis over a normal working lifetime.

#### D. Evaluation Results and Discussion

##### 1. Medical Evaluation

During the initial survey 15 randomly-selected individuals were questioned regarding their general health. Attempts were then made to elicit present symptoms or a past history of respiratory or cutaneous disorders which might be considered occupational in origin. No one related complaints or knew of other men working in his area with health-related problems. Nine individuals reported by the Union as having past or present health complaints were individually interviewed and examined during the two survey periods. One individual was re-examined during the second visit. In three instances men were visited in their homes (one individual had been retired since 1968,

another was on long-term disability, and the third worked the evening shift). Eight of these men complained of present (5) or past dermatitis (3). In four instances, all noted during the initial survey period, moderate cases of definite contact dermatitis traceable to direct contact with MIPA or MIPA contaminated dust were identified.

A single individual complained of headache, epigastric pain, sore throat, and eye irritation when working around MIPA. Another individual was noted during the second survey period to have a chronic eczematous eruption of the left wrist. This individual is atopic and it is felt that his dermatitis most likely represents nickel allergy due to his watchband. The retired worker gave a history of dermatitis definitely related to MIPA exposure, but he has had no further skin problem. The individual on disability was noted to have a chronic scaling (ichthyotic) process involving the legs, keratosis pilaris, and a mild furunculosis of the abdomen and thighs. The latter problem cleared between visits but his skin was still noted to be generally asteatotic (dry). His dermatitis is certainly not occupational in origin. A final individual was noted to have thickened and fissured skin on his finger tips probably largely attributable to pressure and the use of a harsh industrial cleaner.

No evidence or cases were found suggesting that titanium dioxide dust represents any pulmonary or other hazard to employees working in the area covered by this report.

## 2. Environmental Evaluation

During the initial visit five of the nine 50" mills were operational with major maintenance work being performed on two mills. It is during major maintenance work or during spills or leaks in the MIPA lines that the possibility of major exposure occurs. No environmental sampling was accomplished initially since no appropriate sampling or analytical technique was then available for MIPA. The environmental survey was scheduled after the sampling and analytical techniques were developed for MIPA or TEA.

Visual observations during both visits noted that clouds of dust were generated during equipment breakdowns, for example, holes in the gasket of a mill, leaks in the ventilation or bagging system, etc. One particularly dusty operation was noted when an operator opened an "A" bin top on the 5th floor to measure the level of  $TiO_2$ . With the exception of the "A" bin, housekeeping was considerably improved on the final visit. Certain jobs such as maintenance, checking levels of certain bins, operation of equipment (e.g., ventilation, bagger, etc.) needing repair and the use of a broom and shovel for routine housekeeping generate undue amounts of airborne dust.

The environmental survey was conducted on May 30, 1973 while three of the four 60" mills were operational and five of the nine 50" mills were operational; and on the following day while two 60" mills and no 50" mills were operational. No operations using MIPA or TEA were noted, and no major maintenance operations were observed during the survey. Hence, no air samples were obtained for MIPA or TEA. Vinyl-metracel filters were used for obtaining Respirable Dust (Dorr-Oliver cyclone and filter casset) and Total Dust (Millipore Field Monitor) in conjunction with an MSA Model G Vacuum Pump and analyzed by gravimetric (weight) methods. All of the personal samples were used to measure Respirable Dust since the average size of the two products consist of dust in the 0.5 and 8.0 micron range. General Area samples were obtained for Respirable Dust and for Total Dust to obtain data on the amount of respirable and total dust loading in a particular area. All of the samples were collected over long periods of the work day and are assumed to represent an 8-hour time-weighted average. Table A presents all air sample results for Total and Respirable Dust in the Milling area.

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Thirteen personal air samples were obtained for Respirable Dust representing various exposures for Mill Operators, Packers, Maintenance Men, and Laborers. Sample results varied from 0.6 mg/M<sup>3</sup> to 3.7 mg/M<sup>3</sup> the highest being at least 20% below the federal standard for Respirable Dust.

Twelve general area samples were obtained at representative locations in the facility. Where possible, side-by-side samples were obtained for Respirable Dust and Total Dust. The maximum results for Respirable Dust and Total Dust occurred on the 5th floor (50" mill) directly over the "A" Mill Bin and were 10.5 mg/M<sup>3</sup> for Respirable Dust and 15 mg/M<sup>3</sup> for Total Dust. Although the standards were exceeded, general area samples cannot be considered to represent continuous exposure levels since personnel are not exposed to this particular atmosphere except for brief periods of time. All other general area samples were well below the federal standards for Respirable Dust and Total Dust.

Bulk samples of the products were obtained during both visits and analyzed for trace impurities. No impurities were detected in amounts which could be considered as a health hazard to employees.

For completeness, we conducted a limited noise survey. No 8-hour evaluation of any employee's total integrated exposure to noise was performed. Noise levels exceeding the current federal standard of 90 dBA were noted in several areas (e.g., 97 dBA near the mill foreman's office, 105 dBA near the Raymond Mills, 105 dBA near the shakers, etc.). Management was aware of this problem and is implementing a more comprehensive hearing conservation program including hearing protective devices, audiometric exams, and where possible, engineering-out (replacing noisy electrical shakers with mechanical shakers) the noise problem.

E. Recommendations

In view of the above information, the following recommendations are made to provide a more desirable working environment for employees in the area covered by this report. It is felt these recommendations are consistent with good industrial hygiene practices. No recommendations are made concerning safety as this is not the purpose of this report.

a. If MIPA or TEA is reintroduced into the process, appropriate protective clothing should be provided and worn by all employees during operations where there is a possibility of direct contact with these substances.

b. Complete implementation of the hearing conservation program should be accomplished.

c. The mills and ancillary equipment (e.g., ventilation system, filter bags, etc.) warrant the institution of a preventive maintenance program. Prompt attention should be given to maintenance problems (e.g., leak in ventilation system, gaskets, etc.) which give rise to airborne dust, and employees should report such problems to supervisors immediately. To retard the unnecessary accumulation of dust, further installation of walking surface floor gratings should be considered.

d. The use of a vacuum cleaner or vacuum system for cleanup operations would preclude dust from becoming airborne as is now the case with the broom and shovel housekeeping. Serious considerations should be given to reactivate and modify as appropriate the vacuum system which was previously used in the milling area.

e. Respirators for inert or nuisance dust should be provided and worn by employees during those operations which involve exposure to obviously excessive amounts of airborne dust.

TABLE A

Air Sample Results for Total Dust and Respirable Dust in Milling Area  
(mg/M<sup>3</sup> - milligrams of dust per cubic meter of air)

<u>Location and/or Operation</u>	<u>Type of Sample</u>	<u>Sample Number</u>	<u>Date</u>	<u>Liters</u>	<u>mg/M<sup>3</sup> Concentrations</u>
Laborer-50" Bottom Mills	P-RD	U-46	5/31	366.6	0.6
Operator-50" Bottom Mills	P-RD	U-30	5/31	450.8	3.2
Operator-50" Top Mills	P-RD	0-68	5/31	442.6	1.1
Laborer-50" Bottom Mills	P-RD	U-34	5/30	529.2	0.7
Operator-50" Bottom Mills	P-RD	U-26	5/30	567.3	1.1
Operator-50" Top Mills	P-RD	0-27	5/30	549.0	1.2
Laborer-50" Top Mills	P-RD	0-75	5/30	625.7	1.1
Maintenance Man	P-RD	U-14	5/30	463.0	1.2
Operator-60" Mills	P-RD	U-6	5/31	385.5	1.6
Operator-60" Mills	P-RD	U-2	5/30	593.7	0.6
Packer-60" Mills	P-RD	0-69	5/30	603.8	1.5
#54 Packer	P-RD	U-12	5/31	439.6	1.8
#35 Packer	P-RD	U-3	5/31	362.7	3.7
1st Floor-#6 50" Mill	GA-TD	U-31	5/30	479.6	2.3
1st Floor-#6 50" Mill	GA-RD	U-47	5/30	495.6	1.5
2nd Floor-#5 50" Mill	GA-RD	0-16	5/30	520.7	1.4
2nd Floor-#5 50" Mill	GA-TD	U-76	5/30	476.0	4.5
3/4 Fan Floor-#5 50" Mill	GA-RD	U-33	5/30	499.2	0.7
5th Floor-A 50" Mill Bin	GA-TD	U-37	5/30	466.2	16.0
5th Floor-A 50" Mill Bin	GA-RD	U-15	5/30	486.1	10.5
#54 Packing 60" Mill Area	GA-TD	0-5	5/31	369.7	3.5
#54 Packing 60" Mill Area	GA-RD	U-72	5/31	369.7	0.7
#35 Packing 60" Mill Area	GA-TD	U-100	5/31	298.3	4.9
#54 Packing 60" Mill Area	GA-TD	U-36	5/31	537.3	1.2
#54 Packing 60" Mill Area	GA-RD	U-39	5/30	524.6	0.6

P - Personal Sample

GA - General Area Sample

RD - Respirable Dust Sample (Dorr-Oliver Cyclone with filter casset)

TD - Total Dust Sample (Millipore Field Monitor)

" - Inch

Report Prepared By: Raymond L. Hervin, Industrial Hygienist, Project Officer  
James B. Lucas, M.D., Principal Medical Officer

Originating Office: Jerome P. Flesch, Chief, Hazard Evaluation Services Branch

Acknowledgements

Laboratory and Medical Evaluation:

James B. Lucas, M.D., MSB, DTS  
Vernon B. Perone, TB, DL&CD

Environmental Evaluation:

Raymond L. Hervin, Region VII, NIOSH  
George J. Butler, WAOHL, NIOSH  
Jeffrey J. Jaeger, Region VII, NIOSH

Laboratory Analysis:

Raymond Rivera, WAOHL, NIOSH  
Russell H. Hendricks, Ph.D., WAOHL, NIOSH  
R. G. Adler, WAOHL, NIOSH  
Charles Nenadic, P&CAB, DLCD  
Robert W. Kurimo, P&CAB, DLCD  
Robert L. Larkin, P&CAB, DLCD  
Richard Kupel, P&CAB, DLCD