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

#### HEALTH HAZARD EVALUATION DETERMINATION REPORT NO. 74-114-207

### KOPPERS COMPANY, INC. OIL CITY, PENNSYLVANIA, 16301 JULY 1975

#### I. TOXICITY DETERMINATION

It is concluded on the basis of the medical and environmental data collected during the period of this evaluation (January 1975 - April 1975) that exposure to airborne 2, 6-di tertiary buty1-4-methyl phenol (DBPC) had resulted in definite and persistent eye and nose irritation among the chemical operators in the Centrifuge Crystallization Area of the Koppers Company, Inc., Oil City, Pennsylvania. Extensive engineering and ventilation modifications were made between the time of the initial visit on January 16-17, 1975 and the follow-up investigation conducted on April 21-22, 1975. Sample results show that these changes have effectively reduced the concentration of DBPC in the area. Based on the concentrations measured, employee interviews, and professional observations, it appears likely that these modifications will be sufficient to prevent the development of irritative symptoms in present employees under normal operating conditions although the one shift interval which had transpired since completion of these changes is insufficient to definitely conclude that the problem has been entirely eliminated.

#### II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are available upon request from the Hazard Evaluation Services Branch, NIOSH, U.S. Post Office Building, Room 508, 5th and Walnut Streets, Cincinnati, Ohio 45202. Copies have been sent to:

- a) Koppers Company, Inc., Oil City, Pennsylvania
- b) Authorized Representative of Employees
- c) U. S. Department of Labor Region III
- d) NIOSH Region III

For the purpose of informing the approximately 4 "affected employees" this report shall be posted in a prominent place readily accessible to workers for a period of at least 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 an 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.

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The National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized representative of employees regarding exposure of workers to 2, 6-di tertiary butyl-4-methyl phenol (commonly known as 2, 6-di tertiary butyl-p-cresol or DBPC) at Koppers Company, Inc., Oil City, Pennsylvania.

#### IV. HEALTH HAZARD EVALUATION

#### A. Conditions of Use

The survey at the Koppers Company was limited to the Centrifuge Crystallization Building (CCB) where DBPC is purified. The purification process involves the extraction of DBPC from water during which time it goes through a series of crystallization stages. Because DBPC is a solid at room temperature, the purification process requires that the DBPC be heated. Both vapor and dust are therefore present in the area. At the time of the initial NIOSH survey many of the vessels used in the above process opened directly into the room atmosphere. These vessels have now been covered and a new flaker has been installed which has local ventilation. In addition, an uncovered waste product tank (slop tank) in which waste DBPC was remelted prior to storage has been relocated outside the building. Production is continuous throughout the week and utilizes three daily 8-hour shifts.

#### B. Evaluation Methods

#### 1. Environmental Sampling

On the initial survey samples for DBPC were taken on silver membrane filters in series with charcoal tubes. No detectable DBPC was found on the filters. When the charcoal tube samples were desorbed and analyzed by gas chromatography three main peaks appeared. Mass spectrometry confirmed the presence of DBPC as the first of these peaks. The other two peaks could not be positively identified but appeared to be heavier, oxidized forms of DBPC. Since DBPC apparently reacts on charcoal, standards were prepared directly on charcoal to minimize the effect. The sums of the areas of the three major DBPC peaks for each sample were compared to the peak area totals for the standards treated in the same manner. The concentrations reported are the sums of the areas of the three major DBPC peaks for each sample. The results obtained should be considered minimum concentrations.

On the follow-up survey, employee exposures were measured by adsorbing the DBPC onto silica gel tubes and analyzing by gas chromatographic procedures. Representative backup sections from the silica gel tubes were analyzed and found to contain no DBPC. Personal breathing zone samples were taken and area samples were collected at various sites where the DBPC concentration was expected to be the highest. Several simultaneous samples were collected using impingers containing heptane. During sampling, the impingers were refilled with heptane as needed. Prior to analysis by gas chromatography, the impinger samples were evaporated and then diluted to volume with heptane.

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It is felt that the results obtained from the silica gel tubes are more reliable than those obtained from the impingers due to the number of variables associated with the impinger method, e.g., evaporation during sampling and the evaporation and dilution technique used in the analysis. These variables and the fact that collection efficiency tests were not performed on the impingers in relation to DBPC, place some question on the accuracy of the results. It is therefore felt that the concentrations obtained from the silica gel tubes are a better representation of the true concentrations which were present.

#### 2. Medical Evaluation

On the follow-up survey in April 1975 employees were privately asked nondirected questions regarding their health and employment by the NIOSH physician. More specific and directed questions relevant to elicited problems were then asked.

#### C. Evaluation Criteria

DBPC is the technical or commercial grade of BHT (Butalated Hydroxy Toluene). DBPC or BHT is a widely used anti-oxident. It is commonly employed in the food industry as an additive to reduce rancidity and improve stability. From a toxicological point of view, this substance has been considered to be virtually devoid of toxicity. Studies have shown that high dose levels are required to produce evidence of toxicity in animals.(1,2,3) There is little evidence of either acute or chronic effects on humans. While many commercial anti-oxidents are known cutaneous sensitizers, DBPC has not been reported to cause allergic sensitization or skin irritation. A 3-day patch test utilizing commercial grade flaked DBPC failed to elicit any evidence of irritancy when applied to a NIOSH volunteer.

An OSHA standard has not been adopted for this substance. However, the American Conference of Governmental Industrial Hygienist Committee on Threshold Limits 1975 is recommending that a TLV for DBPC be set at 10 mg/M<sup>3</sup>. TLV's or standards for substances are established at levels designed to protect workers occupationally exposed on an 8-hour per day, 40-hour per week basis over a working lifetime.

Because of wide variation in individual susceptibility, some workers may experience discomfort at or below the designated levels. Thus, an evaluation of the work place cannot be based entirely upon comparisons made against such TLV's or standards, as various TLV's and standards do not represent absolute protection of all workers.

#### D. Evaluation Results and Discussions

1. Environmental

On January 16 and 17, 1975 personal breathing zone samples were taken on the CCB operators using silver membrane filters in series with charcoal tubes. Area samples were collected at locations where the highest levels of DBPC were suspected to exist, e.g., near the decanter, flaker and Page 4 - Health Hazard Evaluation Determination 74-114

waste product tank (slop tank). The sample results are shown in Table 1. The results show that the concentration range for the CCB operators was  $4.2 \text{ mg/M}^3$  to  $10.5 \text{ mg/M}^3$ . The highest concentration measured occurred during an eleven minute sampling period above the slop tank. The concentration of DBPC measured was  $619 \text{ mg/M}^3$ .

Personal breathing zone samples were obtained on the CCB operators on the follow-up survey on April 20 and 21. Area samples were taken near the centrifuge, decanter, flaker, packing area and slop tank. Samples were collected on silica gel tubes, with several simultaneous samples being collected using impingers. Sample results are shown in Table 2. The concentration range for the CCB operators was 1.64 mg/M<sup>3</sup> to 2.63 mg/M<sup>3</sup>. The highest area concentration measured was 15.4 mg/M<sup>3</sup>, which occurred during steam cleaning of the centrifuge. All other area samples showed concentrations of less than 6.36 mg/M<sup>3</sup>, with the average concentration being approximately 2 mg/M<sup>3</sup>.

2. Medical (April 1975)

Since only one employee is regularly employed per shift in the Centrifuge Crystallization Building, the number of persons available for medical interviews and examinations were limited to the three consecutive shift employees, the relief operator and one former operator.

These five employees ranged in age from 25 to 31 (average 29) and had been employed by Koppers for an average of 4.7 years (range 4 months to 7 years). The average time as an operator in this plant area was shorter, averaging 2 years (range 10 weeks to 4 years). Only one employee was a female. None had relevant previous employment.

Interviews were initiated in a non-directed manner to elicit general health related complaints and symptoms. More detailed and specific questions relevant to elicited problems were then asked. All five employees reported symptoms (usually burning and/or tearing) of eye irritation. These symptoms were usually experienced at least daily and usually were present for at least half the work shift. Nasal irritation manifested by discharge, stuffiness or bleeding was reported by four of the five employees. Again, this was a nearly constant complaint for the affected workers. No symptoms, however, were reported to be present on the days of the follow-up survey (April 20-21).

Three employees reported skin problems and one of these had a current dermatitis. This individual related a history of atopy (hayfever, asthma or infantile eczema) and the distribution of his lesions was that classically associated with atopic dermatitis. One individual reported a recent, but now resolved, dermatitis that did not have a distribution suggesting occupation causation. The remaining individual had been employed in the area but had experienced no dermatitis problem in the 18 months since transfer. Thus, there was no evidence of a occupational dermatitis problem among currently employed operators. One employee was found to have a potentially serious medical problem for which he is receiving medical attention. This condition pre-dated employment in the area under consideration although it appeared to be definitely exacerbated by work in the Centrifuge Crystallization Area. Page 5 - Health Hazard Evaluation Determination 74-114

This individual no longer works in this area. No other serious or relevant medical problems were elicited or detected among the employees interviewed.

#### 3. Discussion

It is concluded on the basis of environmental and medical data collected that exposure to airborne DBPC had resulted in definite and persistent eye and nose irritation among the chemical operators. The results show that 50% of the samples taken during the initial visit, one of which was a personal sample, exceeded the recommended TLV of 10 mg/M<sup>3</sup>. The interviews showed that employees reported eye and nasal irritation daily. Similar symptoms were also experienced by NIOSH personnel during the initial plant visit.

Prior to the medical and environmental evaluation conducted on April 21-22, 1975 numerous engineering changes had been implemented and additional ventilation installed. The effects of these changes are clearly noted in the concentration levels measured. The results indicate that all but one sample was lower than the 10 mg/M<sup>3</sup> level and that all the levels were significantly lower than those measured on the initial survey. Only one shift had transpired since the completion of these changes making it difficult to definitely conclude that the problem has been eliminated. However, based on the measured concentrations, employee interviews and observation made during the evaluation, it appears likely that the changes will be sufficient to prevent development of irritative symptoms in the employees.

#### V. REFERENCES

- 1. Deichmann, W.B., et.al..<u>Arch. Ind. Health</u>, 11: 93, (1955).
- Brown, W.D., A.R. Johnson and M.W. O'Halloran, <u>Aust. of Exp. Biol.</u>, 37: 533, (1959).
- Creaven, P.J., W.H. Davies, R.T. Williams, J. Pharm Pharmac. 18: 485-489, (1966).

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## Table 1

## CHARCOAL TUBE DETERMINATION FOR DBPC

# KOPPERS COMPANY, INC. OIL CITY, PENNSYLVANIA

January 16-17, 1975

Job or Sample Location	Sample No.	Sample Period	Sample Volume	DBPC Concentration	
			liters	(mg/M <sup>3</sup> )	
CCB Operator	1	16:45-22:45	342	10.5	
Area-Near Decanter	2	18:06-20:01	111	5.4	
Area-Near Flaker	3	18:04-21:20	180	5.0	
Area-Above Slop Tank	4	21:35-22:50	66	62.1	
CCB Operator	5	6:40-10:55	236	5.9	
Area-Above Slop Tank	6	10:21-10:32	6.3	619.0	
CCB Operator	7	10:55-13:49	167	4.2	
Area-Near Decanter	8	12:00-13:45	83	14.5	

## Table 2

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# SILICA GEL TUBE AND IMPINGER DETERMINATION FOR DBPC

## KOPPERS COMPANY, INC. OIL CITY, PENNSYLVANIA

# April 21-22, 1975

Job or Sample Location	Sample No.	Sample Method	Sample Period	Sample <u>Volume</u> (liters)	DBPC Concentration (mg/M <sup>3</sup> )
CCB Operator	1	Silica Gel Tube	15:12-19:30	12.2	1.64
	2	Impinger	15:12-18:47	239	0.25
Area-Beside Centrifuge	3	Silica Gel Tube	15:15-19:14	11.8	2.54
	4	Impinger	15:30-18:55	205	0.05
Area-Near Decanter	5	Silica Gel Tube	15:20-17:53	38.7	3.10
	8	Impinger	15:42-18:53	191	0.52
Area-Packing Area	7	Silica Gel Tube	15:26-19:06	9.60	N.D.
	6	Impinger	15:36-18:58	202	0.15
Area-Near Flaker	9	Silica Gel Tube	15:31-19:09	9.58	1.04
	10	Impinger	15:43-18:50	187	0.80
CCB Operator	11	Silica Gel Tube	19:30-22:10	6.61	1.64
	12	Impinger	18:47-22:10	203	1.82
Area-Beside Centrifuge	13	Silica Gel Tube	19:14-22:29	9.77	2.05
	14	Impinger	18:55-22:29	214	1.17
Area-Near Decanter	15	Silica Gel Tube	17:53-22:26	13.6	2.94
	18	Impinger	18:53-22:26	213	0.85
Area-Packing Area	17	Silica Gel Tube	19:06-22:23	8.60	1.16
	16	Impinger	18:58-22:23	205	0.98
Area-Near Flaker	19	Silica Gel Tube	19:09-22:31	8.84	1.13
	20	Impinger	18:50-22:31	221	0.23
CCB Operator	21	Silica Gel Tube	6:37-10:02	8.45	2.37
	22	Impinger	6:46-10:20	214	2.62
Area-Beside Centrifuge	24	Silica Gel Tube	6:36-10:06	10.0	N.D.
	29	Silica Gel Tube	10:06-13:55	11.7	15.4
Area-Backing Area	23	Silica Gel Tube	6:34-10:04	8.04	3.73
	28	Silica Gel Tube	10:04-13:52	9.29	2.15
Area-Near Flaker	25	Silica Gel Tube	6:37-10:06	9.06	1.10
	30	Silica Gel Tube	10:06-13:55	11.5	6.09
Area-Near Decarter	26	Silica Gel Tube	6:38-10:12	9.44	5.35
	31	Silica Gel Tube	10:15-13:55	10.6	4.72
CCB Operator	27	Silica Gel Tube	10:02-13:57	11.4	2.63
	32	Silica Gel Tube	11:18-13:20	0.1	N.D.
Area-Slop Tank	33	Silica Gel Tube	12:03-13:56	5.70	3.51