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Biochemical Research Department

THE DOW CHEMICAL COMPANY

Subject: INDUSTRIAL HYGIENE SURVEY OF VARIOUS OPERATIONS AT THE CHLORINE CELLS, BLDGS. 261, 196, 137, 295, 236, 270, 303, 207.

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Work by H. Hoyle
E. J. Schneider

D. Hobson 4-30-51

E. J. Schneider 4/10/51

to:

I. F. Harlow, Bldg. 309 (1)
R. M. Hunter, Bldg. 261 (1)
W. R. Perry, Bldg. 261 (1)
Medical Department (1)
Att: H. H. Gay, M. D., Bldg. 256
Safety Department (1)
Att: S. M. MacCutcheon, Bldg. 401

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SUMMARY AND CONCLUSIONS

1. Significant amounts of chlorine, sufficient to cause inflammation and swelling of the respiratory system from short periods of exposure, were found in areas where men were working on and among the chlorine cell series.

2. Men working in these areas have been getting by without severe exposure by using respirators, however, it must be kept in mind that excessive amounts of chlorine above the maximum allowable concentration of 1 p.p.m. for an eight-hour exposure do exist among the cell series.

3. No excessive amounts of chlorine were found in the making of bleach solution at the cell brine plant, 303 building.

4. Excessive concentrations of chlorine occurred in the loading of ton cylinders with liquid chlorine when the delivery line became plugged and insufficient time was taken to purge the connecting lines to the cylinder before removing them.

PLAINTIFF'S EXHIBIT

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5. No excessive amounts of chlorine were found during the normal loading of cylinders and no odor of chlorine was noticed during normal operations to purge, test and load tank cars.

6. Excessive amounts of chlorine and sulfuric acid were found while dumping the sulfuric acid drying tower to the sewer.

7. No excessive amounts of alkali dust were found among the chlorine cell series.

8. No significant amounts of mercury vapor were found at the discharge of the vacuum pumps for the mercury arc rectifiers.

9. Excessive amounts of pitch dust must be considered to exist, since men who are working at the pitch grinding operation do become photo-sensitized and must limit their outdoor activities.

10. Large amounts of graphite dust were found during the loading of plates into the buckets to be impregnated with phenol formaldehyde resin solution. Since the loading operation involves only an hour or so, the exposure to the graphite dust can not be considered excessive.

11. The graphite dust concentrations found in the machine shop were well within the limits for an inert dust.

12. The worker using the band-saw was found to be exposed to more fine dust than workers at the other machines, possibly because there was no spot exhaust ventilation provided.

13. No excessive amounts of formaldehyde or phenol vapors were found during the making of the phenol formaldehyde resin or during the various drumming operations.

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14. The millions of particles per cubic foot of air of asbestos was found to run higher than the maximum allowable concentration of 5 for an eight-hour exposure for the handling of dry asbestos in covering the cell diaphragms. Since the exposure occurs only eighteen times a day for a short period with a total exposure of less than two hours, the amounts of asbestos found cannot be considered excessive.

CHLORINE

I. Significance of Chlorine Exposure

1. For many years a gas concentration of 1 p.p.m. (by volume) has been used as a standard for evaluating workmens' exposures. Recently there has been some expression of opinion that 2 or 3 p.p.m. could be tolerated up to 8 hours daily without adverse effect. Gas concentrations much above 3 p.p.m. unquestionably produce irritation (tissue injury) to the eyes, nose, and throat; concentrations above 10 p.p.m. may cause serious effects on single relatively short exposures. Beginning at about 3 p.p.m. chlorine causes unmistakable pain in the eyes, nose and throat to which very little tolerance develops. This painful action serves as an excellent warning of the presence of harmful concentrations of gas. There appears to be no evidence of chronic effects from repeated exposures at concentrations of less than 2-3 p.p.m. (concentrations having no immediate acute effects). Repeated exposures above 2-3 p.p.m., however, may maintain an irritation of the eyes and respiratory passages, produce an erosion of the teeth, and possibly a nonspecific debility.

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2. To a large extent the data of Table I, II, III, and IV merely give numerical expression to what has been apparent by sensory perception and experience, that excessive gas concentrations are encountered rather frequently if not routinely. Considering the nature of the operations and that much chlorine comes from unpreventable or accidental leaks, it may not be practical to reduce these concentrations of chlorine. Accordingly, it is necessary to emphasize the need for proper respiratory protection, the training of workmen, and the provisions for handling leaks. The results emphasize the desirability of medical examinations to assure the workmen are receiving adequate personal protection. If the men show no evidence of injury that is persistent or frequent, then our principal additional recommendation is that every opportunity to lessen chlorine contamination be utilized.

II. Observation and Presentation of Data

1. The odor of chlorine was ever present throughout the cell buildings and from time to time it was noticed that the men were required to use their respirators in order to go about their work.

2. Air samples were collected at several locations and on different days. The results of the air analyses are collected in Table I and II and can be compared with the accepted maximum allowable concentration of 1 p.p.m. for an eight-hour exposure.

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TABLE I

Vapor Concentration of Chlorine Found
Among the Cell Series in Building 137

Location		p.p.m. (by Volume)	
1. Center aisle between series 45 and 46	(10-4-49)	1.44	and cloudy/raining
2. Center aisle between series 41 and 42	(10-4-49)	0.72	" " "
3. Center aisle between series 37 and 38	(10-4-49)	0.31	" " "
4. Center aisle between series 33 and 34	(10-4-49)	0.31	" " "
5. Between series 45 and 47	(10-4-49)	0.31	" " "
6. Between series 41 and 43	(10-4-49)	2.16	" " "
7. On top series 43	(10-5-49)	1.13	cool and clear
8. Between series 46 and 48	(10-5-49)	6.80	" " "
9. Between series 42 and 44	(10-5-49)	4.00	" " "
10. On top series 46	(10-5-49)	3.30	" " "
11. Between series 35 and 37	(10-5-49)	1.44	" " "
12. On top series 35	(10-5-49)	1.44	" " "
13. Between series 31 and 32	(10-5-49)	2.16	" " "
14. Between series 38 and 40	(10-5-49)	1.13	" " "
15. On top series 36	(10-5-49)	1.13	" " "
16. Between series 32 and 34	(10-5-49)	0.31	" " "
17. Near compressors	(10-5-49)	0.31	" " "
18 Center aisle near 13,14,15,16,17,18 series		0.31	" " "
19. On top series 39 repairing leak	(10-6-49)	2.16	and cloudy /raining
20. Near two mechanics repairing compressor	(10-4-49)	4.40	" " "
21. On top series 46 (when back pressure operator added water)	(10-6-49)	7.30	" " "
22. Between series 15 and 17	(10-6-49)	0.72	" " "
23. On top series 15	(10-6-49)	0.31	" " "
24. Between series 16 and 18	(10-6-49)	1.44	" " "
25. On top series 16	(10-6-49)	0.72	" " "
26. On top series 36 repairing leak	(11-18-49)	3.29	cool and clear

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TABLE II

Vapor Concentration of Chlorine Found Among the Chlorine Cell Series in Building 295

Location		p.p.m. (by Volume)
1. Between series 93 and 95	(11-18-49)	0.36 clear and cool
2. Between series 92 and 94	(11-18-49)	0.36 " " "
3. Between series 93 and 95 and on top	(11-18-49)	0.72 " " "
4. On top series 103	(11-18-49)	1.53 " " "
5. On top series 104	(11-30-49)	1.13 " " "
6. On top series 110	(11-30-49)	0.36 " " "
7. On top series 109	(11-30-49	4.4 " " "
8. On top series 103	(11-30-49)	3.6 " " "
9. On top series 101 (men setting it up)	(11-30-49)	14.8, 9.4 " "
10. On top series 99	(11-30-49)	11.5 " " "
11. On top series 98	(11-30-49)	10.8 " " "
12. Center aisle near series 92, 93, 94, 95	(11-30-49)	2.56 " " "

3. In the chlorinating of the cell caustic for bleaching solution at the cell brine plant no irritating or excessive amounts of chlorine escaped during the normal operation.

The results of air analyses collected during the preparation of the bleaching solution are shown in Table III

TABLE III

Vapor Concentrations of Chlorine Found in the Making of Bleach Solution, Building # 303

Location	p.p.m. Chlorine (by Volume)
1. Platform near tank for making bleach solution. In the fumes at the start of bubbling chlorine through the sodium hydroxide	1.1
2. In the fumes after one-half hour of bubbling	1.1
3. In the fumes after one-hour of bubbling and finishing batch up	1.1

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4. The possibility of exposure to chlorine vapors during the loading of tank cars and cylinders was investigated, sensory perception usually being employed as a measure of exposure. If a good vacuum was pulled on the tank car and the connecting lines purged, there was little chance for exposure when removing the valves and testing the car for moisture. With properly repaired valves and tight connections, there was no exposure during loading.

5. In the loading of cylinders, an inside job, there was more chance for exposure to chlorine. During one visit the delivery line for the liquid chlorine became plugged. In removing the connecting lines, insufficient time was allowed for purging and excessive amounts of chlorine were found to exist.

6. During normal operation of the filling of the cylinders no excessive amounts of chlorine were found. The results of air analyses taken during the loading operation of ton cylinders are collected in Table IV.

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Table IV

Vapor Concentrations of Chlorine Found During the Filling of Ton Cylinders of Liquid Chlorine, Bldg. 270 (11/15/50)

Location	p.p.m. (by volume)
1. Breathing zone of operator as he disconnected purge lines from empty ton cylinder	3.12
2. Breathing zone of operator as he disconnects lines from full ton cylinder of liquid chlorine (line became plugged and insufficient time was allowed for purging)	8.2

7. In the operation of changing the drying towers in the cell buildings, high enough concentrations of chlorine and sulfuric acid were encountered to saturate a respirator.

Table V shows the concentrations of chlorine found during this operation.

SULFURIC ACID (PLUS CHLORINE)

I. Significance of Sulfuric Acid Exposure

1. Sulfuric acid fume or mist has an acute irritating action not too different from that of chlorine. The problem presented by this mixture is practically the same as that presented by chlorine alone. The exposure is short and the concentrations sufficiently low that no great hazard is presented by the operation. It is one that occurs regularly, however, the one can question whether or not it is really necessary.

II. Observation and Presentation of Data

1. The odor of sulfuric acid fumes was masked by the chlorine. Air analyses during the operation showed the presence of considerable acid fumes, however, the exposure was of short duration.

2. The results of the air analyses are collected in Table V and can be compared with the maximum allowable concentration of 0.25 p.p.m. for an eight-hour exposure.

(Table V - page 9)

ST0067416

Table V

Concentrations of Chlorine and Sulfuric Acid Fumes Found During the Emptying of a Drying Tower to the Sewer, Building 137

Location	p.p.m. Cl_2 (by volume)	p.p.m. H_2SO_4 (by volume)
1. Operators breathing zone as he opens valve to release sulfuric acid from tower to sewer (first series of towers)	3.3 (5 min.)	5.7 (5 min.)
2. Area near sewer after the tower was dumped (first series of towers)	1.3	2.3
3. Operators breathing zone as he opens valve to release sulfuric acid from tower to sewer (second series of towers)	13.8 (5 min.)	3.9 (5 min.)
4. Area near sewer after the tower was dumped (second series of towers)	2.9	2.1

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ALKALI DUST (PROBABLY SODIUM CARBONATE)

I. Observations and Presentation of Data

1. No maximum allowable concentration has been established for alkali, however, based on plant experience, no significant amounts of sodium hydroxide were found.

2. The presence of finely dispersed titratable alkali was checked by air analyses among the various cell series and the results are collected in Table VI.

Table VI

Dust Concentration of Sodium Hydroxide Found Among the Chlorine Cells Series in Buildings 137 and 295

Location	Bldg. 137	Mgs./cu.meter as NaOH
1. On top of series 47	(10-6-49)	same as blank
2. Between series 45 and 47	(10-6-49)	"
3. Between series 41 and 43	(10-6-49)	"
4. Between series 50 and 48	(10-6-49)	"
5. Between series 42 and 44	(10-6-49)	"
6. Between series 14 and 16	(11-18-49)	2.44
7. Between series 34 and 36	(11-18-49)	2.44
8. Between series 15 and 17	(11-18-49)	2.18

Table VI (cont'd)
Bldg. 295

9. Between series 92 and 94	(11-18-49)	1.95
10. Between series 95 and 97	(11-18-49)	0.66
11. Between series 109 and 111	(11-18-49)	0.80
12. Between series 104 and 106	(11-18-49)	1.14

MERCURY

I. Observations and Presentation of Data

1. Air is constantly being evacuated from the mercury arc rectifiers and discharged into the rectifier room. The possibility of some mercury vapor being given off was checked by sampling at the outlets of the vacuum pumps. The results of the air analyses are collected in Table VII and can be compared with the maximum allowable concentration of 0.1 mg./cu. meter. These concentrations of mercury have no significance whatever.

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Table VII

Vapor Concentrations of Mercury found in the Rectifier Room, Building 137 (11-13-50)

Location	Conc. Hg. Vapor (by volume)
1. Directly beneath the outlet of the low pressure vacuum pump for G-2 skid of mercury arc rectifiers	<0.006 mgs./cu. meter
2. Directly beneath the outlet of the low pressure vacuum pump for G-1 skid of mercury arc rectifiers	<0.006 mgs./cu. meter
3. Directly beneath the outlet of the low pressure vacuum pump for H-2 skid of mercury arc rectifiers	<0.006 mgs./cu. meter
4. General air sample taken between skids G-1 and H-2. Circulating air shut off for winter conditions	<0.006 mgs./ cu. meter

PITCH

I. Significance of Pitch Exposure

1. Coal tar pitch from many different sources has produced a variety of effects in the skin: photosensitivity; acne and other dermatosis; pigmentations and growths, some of which are benign, others malignant. It is said that about half of the cancers attributable to occupational exposures are due to pitch. The heavier fractions and t ars of some petroleums and of shale oil have similar actions. One obtains the impression from published information that the rather heavy exposures among pitch workers cause a high incidence of skin injuries.

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2. It is apparent that the men handling pitch in the chlorine cells come in direct contact with the material, resulting in prolonged and repeated contacts upon some portions of the body. The data in Table VIII indicate a moderately dirty atmosphere.

3. The data in Table IX represent counts of small particles, roughly of particle size 0.1 to 5 microns which may be inhaled. This data indicates that relatively small amounts of pitch dust are being inhaled. Since the literature contains no reference to toxic effects attributable to inhalation, we are not greatly concerned about inhalation of pitch dust.

4. Excessive skin contact with pitch dust is to be controlled by arrangement and design of the process to eliminate manual handling and dispersion of dust, by personal protection of workmen, and measures to assure a high degree of personal cleanliness. The clothing and bath requirements on these jobs have been indicated. It is recommended that the men working directly with pitch be given medical examinations at regular intervals.

II. Observations and Presentation of Data

1. Several exhaust hoods had been installed to control the dust exposure when grinding pitch. The men working on the pitch grinding equipment, however, through known experiences, are apparently exposed to amounts of pitch sufficient to cause photosensitivity.

2. The results of air analyses taken in the worker's breathing zone and in the work area during various operations encountered in pitch grinding are collected in Table VIII.

Table VIII

Dust Concentrations of Pitch Found During the Grinding and Handling Operations in Preparation of Making Cell Cement - Building 196

Location	Conc. Mgs./cu. meter
1. Breathing zone of worker as he opens metal drum of pitch tar and breaks up the contents	63
2. Breathing zone of worker as he shovels broken pieces of pitch into the grinder and dumps buckets of pitch into mills	306
3. Breathing zone of worker as he rakes pulverized pitch from the cyclone and shovels it into the buckets	94
4. Breathing zone of worker as he sweeps area after grinding and filling buckets	453
5. Breathing zone of worker as he operates the cable hoist to dump bucket of pulverized pitch into hopper for the mixer	209,249

3. The results of dust counts taken in the general area and during the various pitch grinding operations are shown in Table IX.

(Table IX - page 13)

ST006750

Table IX

Dust Concentrations Found During the Various Pitch grinding operations and in the General Area

Location (Breathing zone samples taken whenever possible)	m. p. c. f. (average of several counts)
1.Shaking out broken pitch from metal drum	5
2. Breaking up lumps	7
3. Shoveling broken up pitch into grinder	8
4. Dumping buckets of ground pitch to mills	5
5. Sweeping up area where pitch is ground	7
6. Raking out pulverized pitch	5
7. Filling buckets with pulverized pitch	5
8. Sweeping area where buckets are filled	2
9. Dumping bucket to mixer	5
10. Gen. atmosphere near foreman's desk	5
11. Area in front of small mixer while dumping cement to the small mixer with pitch	4
12. Area in front of small mixer while dumping the pitch cement mix	4
13. Area in front of small mixer with men working on poured casting	5
14. Area of building where men are working to prepare the cell forms	5

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GRAPHITE DUST

I. Significance of Graphite Dust Exposures

1. There are a few reports of lung injury (pneumoconiosis) among persons working with graphite. Nearly all reports have dealt with natural graphite containing an appreciable amount of other minerals so that it is not definite that graphite dust alone has an adverse effect.

2. It is apparent that considerable amounts of graphite are dispersed in the air, but the counts of particles susceptible to inhalation fail to indicate any exposures that are questionable. If workmen were regularly and uniformly exposed to counts of more than 50,000,000 particles per cubic foot, correction would be called for.

II. Observations and Presentation of Data

1. A dusty atmosphere was created when a worker used an air hose to remove the loose graphite from the plates before loading. There was still sufficient loose graphite remaining on the plates to make the loading of them very dusty.

2. The results of air analyses made during the loading operations are shown in Table X.

Table X

Dust Concentrations of Graphite Found During the Loading of Plates into the Buckets in Preparation for Pregnating with P.P., Bldg. 261

Location	Dust Conc. : Mg./cu. meter
1. Breathing zone of worker blowing loose graphite off a stack of plates with an air hose (room closed up for winter conditions)	2260
2. Breathing zones of two workers as they load a bucket with graphite plates	2870

3. Several dust counts were taken during the plate loading and in the general atmosphere. The results of these counts are shown in Table XI. These values can be compared with the maximum allowable concentration of 50 m.p.c.f. for an inert dust.

4. Several dust counts were taken in the machine shop, both during the operation of the machines and in the general atmosphere through the area. The results of these counts are shown in Table XI also.

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Table XI

Dust Concentrations of Graphite Found During the Loading of Plates and Various Operations in the Machine Shop.

Treating Room

Location (Sample taken in the breathing zone of worker whenever possible)		m.p.c.f. (average of several counts)
1. Blowing the loose graphite off the plates before loading them		50
2. General atmosphere in the room after blowing		35
3. Piling the plates into the buckets		50
4. General atmosphere of the treating room after finishing the loading of the plates	10 min.	20.1
	15 min.	28.3
	20 min.	35.2
	30 min.	30.8
	45 min.	41.0
5. General atmosphere in the treating room in the morning when the plates are unloaded		2.0

Machine Shop

6. General atmosphere in the machine shop early in the morning before work is started	7
7. Cutting corners off of boards at band saw	20
8. Running plates through bevel machine	8
9. Near new machine for grooving boards	10
10. Near old machine for grooving boards	9
11. Placing boards in machines	8
12. Removing boards from machines	9
13. Where operator sits after loading machines	10
14. Blowing small area from machines so board is locked in	11
15. Blowing machine off for cleaning	10
16. Sweeping up area around machines	8

(Table cont'd on page 16)

ST0006753

Table XI -(cont'd)

17.	General atmosphere near foreman's desk	8
18.	General atmosphere near crib	5
19.	General atmosphere other end of shop	5
20.	General atmosphere office area	4
21	Janitor sweeping floor	5

FORMALDEHYDE

I. Significance of Formaldehyde Exposures

1. None of the exposures measured during normal operation were excessive.

II. Observations and Presentation of Data

1. In the making of the phenol formaldehyde resin, the odor of formaldehyde was noticed throughout the room, however, only during the blowing of the mixing tank was there evidence of eye irritation.

2. In all cases where air analyses were made, the concentration of formaldehyde found was below the maximum allowable concentration of 5 p.p.m. The results of air analyses are collected in Table XII.

PHENOL

I. Significance of Phenol Exposures

1. None of the exposures measured during normal operation were excessive.

II. Observations and Presentation of Data

1. Very little odor of phenol was noticed during the various operations of making phenol formaldehyde resin. The results of the air analyses can be compared with the concentration of 10 p.p.m. phenol found through past company experience to be an acceptable limit.

2. Table XII also shows the results of air analyses for phenol concentration.

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Table XII

Vapor Concentrations of Formaldehyde and Phenol Found During Various Operations of the Phenol Formaldehyde Resin Process, Building 236

Location (Winter conditions - doors and windows closed)	p.p.m. Formaldehyde (by volume)	p.p.m. Phenol (by volum
1. General air sample taken in front of reactor and near operator's desk (reactor up to temp.)	1.0	0.40
2. From an elevated platform between the reactor and mixing tank (reactor up to temp.)	1.0	0.87
3. Next to the mixing tank and operator's desk	0.44	
4. Near the mixing tank as phenol was blown in from trailer outside		0.69
5. Near the mixing tank as formaldehyde was pumped in from storage tank	1.27	
6. Near the mixing tank as air was blown to mix contents	2.8, 2.6	1.04
7. Near the mixing tank and operator's desk after blowing had stopped	4.0	
8. Near the vacuum still (operating) in the area where operator spends considerable time making insulating plugs	1.5	1.19
9. Breathing zone of operator filling 100 gal. drum with evaporated P.F. solution	2.9	1.11
10. Breathing zone of operator filling four 50-gal. drums with neutralized and evaporated P.F. solution for the Texas Division	2.4	0.87
11. Operators breathing zone filling six 50 gal. drums of formaldehyde for interplant use. (work done outside on cold, windy day)	.60	

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ASBESTOS

I. Observations and Presentation of Data

1. The handling of dry asbestos in making up a slurry of caustic, water and asbestos does offer an exposure to finely divided particles of asbestos.

2. The results of dust counts taken in the breathing zone of a worker as he weighs, dumps, and stirs the asbestos into the slurry are shown in Table XIII. These values can be compared with the maximum allowable concentration of 5 m.p.c.f. for an eight-hour exposure. None of the exposures measured during normal operation were excessive since the duration of exposure is short.

Table XIII

Dust Concentrations Found During the Handling of Dry Asbestos in the Covering of Cell Diaphragms

Location (samples taken in worker's breathing zone)	m.p.c.f. (average of several counts)
1. Dumping bag of weighed asbestos (48 lbs.) to slurry tank	8
2. Stirring and mixing the asbestos with water	10
3. Weighing out a bag of asbestos	5

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