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Biochemical Research Laboratory
The Dow Chemical Company

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EVALUATION OF CHEMICAL EXPOSURES
RECEIVED BY R. R. SPENCER OF
COATINGS TECHNICAL SERVICE,
433 BUILDING

File: T2.1-1-~~55~~ (F)
Chg.: 1219
Date: 1-22-58
By: J. E. Peterson

Signed J E Peterson Checked H R Hoyle

Date 1-29-58 Date 1-30-58

PROBLEM

Recently, R. R. Spencer has become ill. The Environmental Research Laboratory was requested to determine chemical exposures received by him, and to assess these data.

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CONCLUSIONS

1. Exposures to airborne materials during the formulation, mixing, and calendering of vinyl asbestos tile in 433 Building were evaluated on 12-23-54 and on 1-15-58. Results of these evaluations are used to assess exposures received by R. R. Spencer during his work with this material.

2. From December 1953 to December 1954, R. R. Spencer worked with vinyl asbestos tile formulations, and in the course of that work was occasionally exposed to somewhat excessive concentrations of airborne asbestos.

During this period of time exposure to lead occurred, but his blood lead level on 3-7-55 was only 0.024 mg./100 cc. blood, a normal figure. Exposures to cadmium during this period were to airborne concentrations of "$\leq$ 0.7 mg./m^3" at intermittent periods. No effect is expected as a result of these exposures.

3. From the first part of 1955 to late 1956 Mr. Spencer worked mostly with latex in concrete, and exposures to vinyl-asbestos tile ingredients were reduced accordingly.

4. From the last part of 1956 until the present he has been working with vinyl-asbestos tile formulations in a supervisory capacity. During this work he was probably exposed a maximum of 1-2 days per week to airborne dust concentrations of less than 3 mppcf of a material analyzing 20-30% asbestos, less than 5% SiO_2, and about 0.02% cadmium. No effect can be expected from such exposure.

5. If Mr. Spencer's difficulty is the result of chemical exposure, the causitive agent is unknown at present. Further air analyses are to be made during a time when chlorinated polyethylene is used as the resin binder in the tile formulations.

PRESENTATION OF DATA

R. R. Spencer has been ill with a lung difficulty, and overexposure to chemicals encountered during the formulation, mixing, and calendering of vinyl-asbestos tile formulations was suspected to be the cause of his illness. The Environmental Research Laboratory was requested to determine and evaluate his exposures.

On 12-23-54 an environmental survey of the vinyl-asbestos tile formulating operation was made by S. R. Johann; the results of this work were reported on 5-5-55 (File Number, T2.1-1-32). This survey found that air concentrations of "inerts" (asbestos plus calcium carbonate), barium, and lead were too high for repeated 8-hour exposures, and even though exposures were not that prolonged, recommended the installation of local exhaust ventilation. Cadmium was determined in the air samples, but in all cases the amount present was below the limit of sensitivity of the analytical technique employed, leading to air concentration figures of "less than" 0.66 mg./m^3 and "less than" 0.45 mg./m^3.

As a result of this investigation several changes were made. First, the use of lead and barium compounds in the formulation was sharply curtailed. Second, operational techniques were changed so that each batch was completely formulated before mixing in the Banbury or Baker-Perkins machines, and mixing in these enclosed machines was always to be done prior to

Third, canopy hoods were installed over the large 2-roll mill and over the calender, but not over the small 2-roll mill usually used for preliminary compounding of these formulations. Finally, the Building Products group recently moved into new quarters where a bench-type hood is always available to control dust from dry mixing.

In connection with the environmental survey of December 1954, samples were taken for blood-lead determinations for the men involved on this project. R. R. Spencer's blood lead concentration was found to be 0.024 mg./100 cc. of blood, a normal figure, indicating insignificant exposure to lead. The other two men involved also had normal blood lead values.

On 1-15-58 a second environmental survey of the vinyl-asbestos tile operations was made, partly to assess the value of indicated changes in reducing exposures of personnel, and partly to gain more insight into the chemical exposures that R. R. Spencer may have received recently.

The ingredients used in vinyl-asbestos tile formulations have adhered quite well to the same basic recipe for over a year.

The recipe is as follows:

Material	Weight Ratio
Resin - May be chlorinated polyethylene or resin 2716, the copolymer of 15% vinylidene chloride, 85% vinyl chloride.	17.5
Dioctyl phthalate or tricresyl phosphate	2.25
Monoplex S-38 - An epoxidized oil purchased from Rohm and Haas.	2.25
Metasap 624 - Contains cadmium laurate	1.5
Aluminium stearate	0.1
Paraffin wax	0.1
Lesimit - Calcium carbonate	39.8
No. 18 graining sand - A very fine sand	12.5
Titanox RA50- Titanium dioxide	5.0
Asbestos shorts, type 7M	19.0

With the exception of dioctyl phthalate and monoplex S-38, which are liquids, all of these materials are dry powders, and normally are weighed into a stainless steel mixing bowl in the open. This operation takes about 5 minutes. The mixing bowl is then placed under a mixer within a hood, mixed for a few minutes, and then the two liquids are added. After further mixing, the batch (which is still a dry powder) is poured into a paper bag held within the hood.

When it is done, weighing and blending of the ingredients takes place at a maximum frequency of about 3-half-days per week; an average frequency is difficult to establish because two or three weeks may pass with no activity in this area at all. Mr. Spencer normally would be involved in about 10% of this work which is usually done by a lab technician.

Dry powder from the paper bag is poured directly into the Baker-Perkins or Banbury mixer - usually the Banbury. Here the material is forced into a heated mixing chamber with an air-powered ram and is mixed for about two minutes. The resulting mass is semi-plastic, and is removed (sometimes with difficulty) from the mixer and carried to the differential speed heated (200-300°F.) 2-roll mill. On this mill it is further blended and occasionally marbilizi: chips are added. Such blending may take from 2 or 3 minutes to a half-hour depending upon the difficulties encountered.

After being thoroughly mixed on the 2-roll mill the plastic mass is carried to the calender (basically a cooler heated 2-roll mill) a few feet away. Here the material is squeezed to a pre-determined thickness by a pass through the rolls; the surface of the resulting strip is improved by a second pass through this machine. The strip of tile material is then cut into pieces of the correct size for testing with a shear. From Banbury mixer to finished pieces of tile may take from 15 minutes to an hour or so for a single batch.

The maximum frequency of this job is about the same as for weighing and blending, 3 half-days per week, and again, an average frequency is almost impossible to establish. For reasons of safety, two men always work together in these operations; Mr. Spencer has been associated with about 80% of this work since the latter part of 1956.

On 1-15-58 several air analyses were made during vinyl-asbestos tile manufacture. Air sampling equipment used was the Bausch and Lomb dust counting microscope and the electrostatic precipitator. Results of these air analyses are presented in Table I. Samples 1-11 were taken with the B and L dust counting microscope and the concentrations are expressed in terms of millions of particles per cubic foot of air. (mppcf). Samples 12-14 were taken with the electrostatic precipitator, and normally concentrations would be expressed as milligrams of air contaminant per cubic meter of air ($mg./m^3$), but the samples were unfortunately of too short duration to obtain weighable quantities of dust.

Table I

Sample No.	Description	Dust Concentration, mppcf
1	An air sample taken directly over a paper bag of dry materials shaken to produce dust. This sample was mainly to establish the size range of the airborne particles.	Most particles ≤ 5μ in diamete average about 2-3 μ
2	Breathing zone sample as a paper bag of formulation was dumped into the Banbury mixer.	3.2
3	Sample of fume from the hot semi-plastic mass as it was withdrawn from the mixer, not a breathing zone sample.	0.7
4	Breathing zone of a man removing the semi-plastic mass from the Banbury mixer with steel picks.	1.0
5	Breathing zone while working the material on the 2-roll mill.	0.9
6	Breathing zone while working the material on the 2-roll mill.	0.2
7	Breathing zone of man as he put the material through the calender.	0.7
8	Breathing zone while cutting the tile to size on the shear.	0.5
9	Room air in the office.	0.2
10	Breathing zone of lab technician as he added dry asbestos fiber to the mixing container on a scale in the laboratory.	1.4

Sample No.	Description	Length of Time of Sample	Dust Concentration, MPPCF / Dust Conc. mg./m.^{3}
11	Immediately outside of the bench hood where the dry batch of material was being mixed.		0.5
12	Electrostatic precipitator sample in the breathing zone while formulation being mixed in the Banbury.	2 min.	Too little to
13	Breathing zone while working the formulation on the 2-roll mill.		Too little to measure.
14	Sample taken in bench hood over the container where the dry mixture was being stirred. This sample was taken only to determine the relative proportions of the dust constituents in air.		$CaCO_3$ - Main Constitue Asbestos - 20-30% SiO_2 <5% Cd 0.02%

The resin used for the tile formulation involved in the work described in Table I was resin 2716, consisting of the polymer made from 15% vinylidene chloride, 85% vinyl chloride. Analysis of Sample 14 was by x-ray diffraction and emission spectrograph; the organic materials are not "seen" by this method.

The dust concentrations shown in Table I may be compared with the appropriate Industrial Hygiene Standards, listed in Table II. Industrial Hygiene Standards are concentrations which may be inhaled as much as 8 hours per day, 5 days per week indefinitely without ill effect.

Table II

Industrial Hygiene Standards

Material	Standard
Asbestos	5.0 mppcf
Silica (quartz)	5.0 mppcf
Cadmium	0.10 mg./m^3
Calcium Carbonate	15.0 mg./m^3
Resin 2716	probably 15.0 mg./m^3

An examination of Tables I and II readily shows that at no time were the standards for asbestos or silica exceeded. Since the dust counting microscope determines the number, not the weigh of particles in the air some assumptions must be made before the cadmium exposure can be evaluated: (1) assume that the dust encountered near the Banbury mixer, 2-roll mill and callender had the same particle-size distribution as the dust of the dry mixture (confirmed by dark-field microscopic examination); (2) assume the dust particles were spherical with an average diameter of 2.5μ; (3) assume the density of the particles was approximately 2.0 g./cc.

Using these assumptions, the weight concentration of dust correspon to the highest observed particle concentration (3.2 mppcf) would be $\doteq$ 1.85 mg./m.^{3}. Then, assuming that the particles were 0.02% cadmium the air concentration of cadmium was about 0.0004 mg./m.^{3}, well below the 0.10 mg./m^3 Standard, especially considering that all of the assumptions made were conservative.

Thermal decomposition products of the resin and plasticizers used could conceivably be the cause of trouble except that a great amount of experience at Dow and at other companies with these materials has shown that no adverse effects are to be expected even under much worse conditions than have been prevalent in 433 Building.

Remaining as a possibility is the dust and/or thermal decomposition products from chlorinated polyethylene, a new material. A survey will be made when this material is again used in vinyl-asbestos tile formulations in order to determine what materials are inhaled, and in what concentrations. Also, this dust, along with the dust of other materials, is soon to be investigated by the Toxicology Laboratory to determine the degree of irritation caused by sub-dermal injections. This investigation should help to decide whether or not Mr. Spencer's lung injury could have been caused by the resins used in vinyl-asbestos tile formulations.

The bench hood used in the laboratory for dry mixing was evaluated by measuring air velocities at the face of the hood with an Anemometer Air Meter. The attached "Hood Survey Data Sheet" is self explanatory regarding findings and recommendations.

HOOD SURVEY DATA

FILE NUMBER	BUILDING NUMBER	DATE	TYPE OF HOOD
T21-1-92	437	1/15/52	LAB BENCH

HOOD LOCATION DESIGNATION: BUILDING PRODUCTS LAB, PTS

INTERNAL BAFFLE	EXTERNAL BAFFLE	CHEMICALS HANDLED IN THIS HOOD
YES	NO	ASBESTOS, PVC, PLASTICIZERS, ETC, CEMENT, SOLVENT

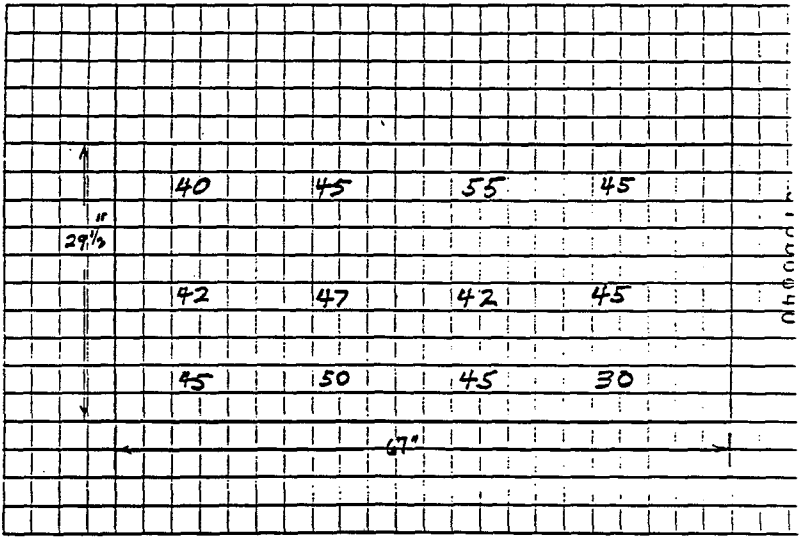
OTHER HOODS CONNECTED TO THE SAME EXHAUST SYSTEM: SOVENS

SOURCES OF AIR DISTURBANCE EXTERNAL TO THIS HOOD: AIR DIFFUSER INLET ABOUT 8 FEET FROM FRONT OF HOOD

REMARKS:

RECOMMENDED MEAN FACE VELOCITY FOR THIS HOOD 80 F. P. M., DOOR OPEN 29½

RECOMMENDED EXHAUST RATE FOR THIS HOOD 1100 C. F. M.



HOOD CONDITIONS DURING THE SURVEY

	MAXIMUM	MINIMUM	MEAN	VARI.
ACTUAL FACE VELOCITIES	55 F.P.M.	30 F.P.M.	44 F.P.M.	32 %
HOOD FACE AREA DURING SURVEY	13.7 SQ. FT.			
EXHAUST RATE DURING SURVEY	605 C.F.M.			

MAXIMUM OPENING: HEIGHT 29½ IN., WIDTH 67 IN. MAXIMUM HOOD FACE AREA 13.7 SQ.

INSTRUMENT USED FOR AIR VELOCITY MEASUREMENTS	SERIAL NUMBER	SURVEYOR
ANEMOTHERM AIR METER	5259	J.E.P.

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HOOD SURVEY DATA

FILE NUMBER	BUILDING NUMBER	DATE	TYPE OF HOOD
TJ-1-32	Y33	11/15/58	LAB BENCH

HOOD LOCATION, DESIGNATION: BUILDING PRODUCTS LAB, PTS

INTERNAL BAFFLE?	EXTERNAL BAFFLE?	CHEMICALS HANDLED IN THIS HOOD

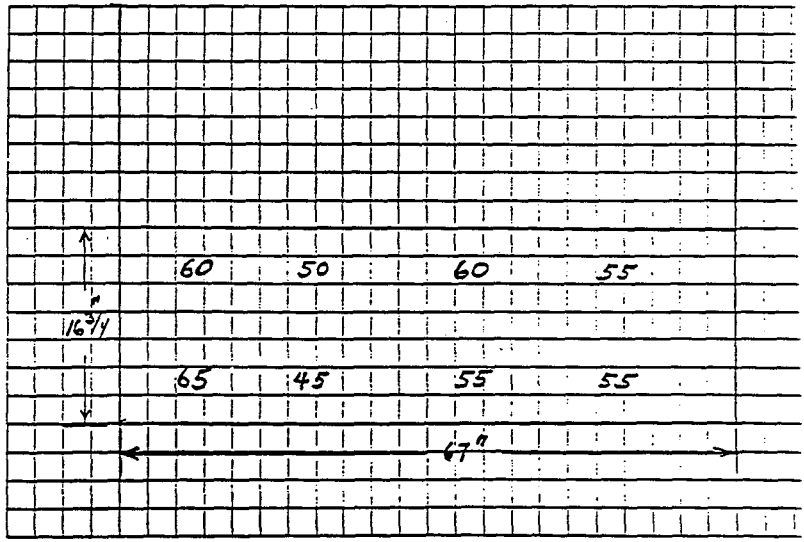
OTHER HOODS CONNECTED TO THE SAME EXHAUST SYSTEM:

SOURCES OF AIR DISTURBANCE EXTERNAL TO THIS HOOD:

REMARKS:

RECOMMENDED MEAN FACE VELOCITY FOR THIS HOOD 80 F. P. M. DOOR OPEN WIDE, 29 1/2

RECOMMENDED EXHAUST RATE FOR THIS HOOD 1100 C. F. M.



HOOD CONDITIONS DURING THE SURVEY

	MAXIMUM	MINIMUM	MEAN	VARI.
ACTUAL FACE VELOCITIES	60 F.P.M.	45 F.P.M.	56 F.P.M.	45 (1)
HOOD FACE AREA DURING SURVEY	7.8 SQ. FT.			
EXHAUST RATE DURING SURVEY	434 C.F.M.			

MAXIMUM OPENING: HEIGHT 29 1/2 IN., WIDTH 67 IN. MAXIMUM HOOD FACE AREA 13.7 SQ

INSTRUMENT USED FOR AIR VELOCITY MEASUREMENTS	SERIAL NUMBER	SURVEYOR
ANEMOTHERM AIR METER	52.59	J.E.P.

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I am an author of and have read this report comprising 13 pages with 2 pages of drawings, photographs, graphs, and checked the data herein against the original entries under Biochemical Laboratory File Number T2.1-1-65

Signature [signature] Date 2/6/58

Signature ______________________ Date ________

I finished typing this report on 1-29-58 comprising 13 pages and placed therewith 2 pages of drawings, photographs, graphs from an original draft given me by J. E. Peterson on 1-27-58.

I have placed in the plant mail 5 copies of this report for transmittal to Please refer to the Distribution list of this repor

Signature [signature] Date 2-6-58

UNIT INDEX

Possible chemical exposures received by R. R. Spencer of Coatings Technical Service while working with vinyl-asbestos tile formulations are evaluated as possible causes of his lung injury. No evidence leading to the determination of a causitive agent was found, but plans were made for another survey to be performed when chlorinated polyethylene is used as the resin in a tile formulation, and dust of this material will also be investigated further by the Toxicology Laboratory.

DISTRIBUTION

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