

Biochemical Research Laboratory

The Dow Chemical Company

VAPOR EXPOSURES TO VINYL CHLORIDE
AND VINYLIDENE CHLORIDE ENCOUNTERED
BY REACTOR AND STILL OPERATORS,
POLYMER #1 AND #2, SARAN PRODUCTION,
BUILDING 262

File: T64.4-2-2

Date: March 10, 1965

By: E. J. Schneider

Signed

E. J. Schneider

Date

3/11/65

Checked

H. H. Hyle

Date

3/13/65

Material Produced Pursuant

Case No. 90-4837

San Antonio, TX

Smith v. The Dow Chemical Company

Case No. 94-CV-0393 S(H)

Western District of Texas

PROBLEM

A twelve point electro-conductivity ~~hydrocarbon~~ hydrocarbon analyzer has been used to continuously monitor vapor concentrations of vinyl chloride and vinylidene chloride in operator's work areas of the Saran Production Plant for several years. The equipment has provided supervision with a daily record of the vapor concentrations of vinyl/vinylidene chloride encountered by the operators as well as an indication of leaking equipment. Until recently, however, there has not been available a satisfactory method of compiling the data to show the exposure pattern of the operators to vinyl chloride and vinylidene chloride. In the early part of 1962 the Environmental Research Laboratory acquired data processing equipment which could be used in conjunction with the electro-conductivity analyzer and the Burroughs digital computer. During the months of January through the middle of June, 1962, and again during the months of January through April, 1963, environmental studies were conducted at the Saran Production Plant using the new data processing equipment.

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R&S 000441

CONCLUSIONS

1. Reactor operators (kettle men) of the Polymer #1 section do encounter at times high concentrations of vinyl/vinylidene chloride. Time-weighting the exposures resulted in values in excess of recently proposed safe limits for repeated exposures.
2. The high concentrations do not correlate with increased production but relate more directly to operating techniques and maintenance of equipment. A daily investigation of the cause of the high concentrations over a trial period of time by supervision did produce a satisfactory reduction in the operator's exposure.
3. Time-weighted exposures to vinyl/vinylidene chloride encountered by reactor operators (kettle men) of the Polymer #2 section and the still operators of both sections were found to be within acceptable levels.
4. Results of physical examinations of the operators conducted by the Medical Research Laboratory at the time of the 1963 environmental survey are to be reported separately.

REASONS FOR THE ENVIRONMENTAL STUDY

Vinyl chloride and vinylidene chloride monomers are reacted in the presence of a catalyst to produce saran polymer. Throughout various stages of manufacture, reactor operators

(kettle men) and still operators are subject to possible exposures to the two monomers. Because both vinyl chloride and vinylidene chloride are toxic to the liver and kidneys there is a definite need to evaluate the operator's exposure and to control them to within acceptable limits.

The Environmental Research Laboratory began making surveys with portable air sampling equipment in 1950 with subsequent surveys in 1951, 53 and 55. Results of these surveys prompted supervision to install a continuous monitoring system for detecting and recording concentrations of vinyl chloride/vinylidene chloride in the general work areas for the operators.

The monitoring system installed consists of an analyzer and recorder located in a separate room outside the main plant with twelve air sampling lines running out from the analyzer to the operating areas. The analyzer has a combustion furnace to decompose the halogenated hydrocarbon, scrubbing absorbers to mix water with the free hydrogen chloride and/or chlorine formed by that decomposition and two six-point Dynalog recorders to record the conductivity of the solution formed. Arrangements were made for the Instrument Systems Research group to be responsible for weekly maintenance of the analyzer and for the Environmental Research Laboratory to check the calibration of the analyzer approximately every six months. This has been done since 1958.

R&S 000443

In determining the vapor concentrations of vinyl chloride and/or vinylidene chloride in the general atmosphere with the halogen analyzer it was not possible to record separately the concentrations of each monomer. The analyzer is nonspecific and is able to only analyze for total halogen content. Thus the instrument was calibrated to report all the results as vinyl chloride. The chronic vapor toxicity of these two materials is about proportional to the number of chlorine atoms in each molecule.

After several months of operation, there was definite evidence (as indicated by the daily charts) that for periods of time lasting a few minutes up to several hours, concentrations of vapors recorded as vinyl chloride in excess of 100 ppm (parts per million by volume in air) existed in various work areas. It, however, has been an unrealistic task to attempt to visually and manually integrate the data in order to time-weight the exposures of the operators so as to evaluate the possible hazard.

Early in 1962 the Environmental Research Laboratory acquired semi-portable analog-to-digital recording equipment which would record each conductivity reading along with time in days, hours and minutes. The data recording system consists of a specially modified Brown recorder, a Datex Encoder and Programmer and a Friden paper tape punch. The data are punched in a code and format suitable for direct entry to the Computations Laboratory B-220 digital computer. The computer was programmed to provide summaries of the concentrations of vinyl/vinylidene

R&S 000444

chloride as vinyl chloride at the twelve air sampling locations in terms of average concentrations and percentage of time above various levels for each of the three daily shifts and for the complete day. Weekly and monthly summaries of this information were also obtained. Later, programming provided time-weighted average concentrations and percentage of time above various levels for the operator's exposures.

The new data recording equipment was connected to the continuous monitoring system during the months of January-June, 1962, and again during the months of January-April, 1963. Accurate and acceptable data were obtained within these periods.

PRESENTATION OF DATA

Nine of the twelve air sampling locations were chosen to monitor the concentrations of vinyl/vinylidene chloride in areas most frequented by the Saran operators. The other three air sampling locations were used for the Soluble Saran section in other parts of the building. Data from these three locations have not been included in this report.

It was not practical to attempt to monitor the peak exposures which the operators can encounter when cleaning valves on the bottom of kettles, changing filter sacks or replacing safeties in lines. The air sampling points do monitor air that the operators breath the major part of the time. Tables I, II and III indicate the locations of the nine sample points and the

R&S 000445

Biochemical Research Laboratory
T64.4-2-2
Page 6

approximate time spent by the Polymer #1 and #2 reactor and still
operators in each of the locations.

R&S 000446

Down Chemical Confidential Material Produced Pursuant
To Protective Order
Re: Down Chemical Company Case No. 89-4837
U.S. District Court
Southern District of New York
Produced Pursuant to Protective Order
Case No. 89-4837 (S.D.N.Y.)
Western District of New York

Table I

APPROXIMATE TIME SPENT BY POLYMER #1 KETTLE MEN IN THEIR
VARIOUS WORK AREAS, BUILDING 262

<u>Analyzer Sample Point</u>	<u>Location</u>	<u>Approximate Time Spent in Area</u>
1	Base of slurry tanks, ground floor level (attends compression area and other duties).	12%
7	Control panel and desk area, third floor level (loads kettles, checks charts, etc.).	31%
9	Area of the scales in the Receiver Room, third floor level (filling the receivers with monomers and attending the pumps).	20%
12	Area of the slurry tanks and base of kettles, second floor level (dropping the contents of kettles to the slurry tanks and cleaning the valves at the bottom of kettles).	25%
-	Lunch room.	12%
TOTAL		100%

R&S 000447

Deu: Chemical Confidential Material Produced Pursuant
To Protective Order
Exhibit 1, Case No. 89-4837
Subpoena Duces Tecum
Subpoena Duces Tecum
Case No. 89-4837 (n)
Western District of New York

Table II

APPROXIMATE TIME SPENT BY POLYMER #2 KETTLE MEN IN THEIR
VARIOUS WORK AREAS, BUILDING 262

<u>Analyzer Sample Point</u>	<u>Location</u>	<u>Approximate Time Spent in Area</u>
2	Area near #10 scales in the Receiver Room (filling the receivers with monomer).	6%
4	Area near #13 scales in the Receiver Room (filling the receivers with monomer and changing the filter sock).	6%
6	Area near top #4 drier and kettle trap (dropping the contents of kettles to the drier and cleaning the valves at the bottom of the kettles).	20%
10	Area of operators desk near #24 and #27 kettles (loads kettles, checks charts, etc.).	46%
-	Lunch room.	12%
-	Other duties out of the main operating areas.	10%
TOTAL		100%

Best Chemical Confidential Material Produced Pursuant
To Court Order No. 63-4837
Best Chemical Company
Grand Central Station
Western District of New York

R&S 000448

Table III

APPROXIMATE TIME SPENT BY THE STILL OPERATORS IN THEIR
VARIOUS WORK AREAS, BUILDING 262

<u>Analyzer Sample Point</u>	<u>Locations</u>	<u>Approximate Time Spent in Area</u>
4	Area near #13 scales in the Polymer #2 Receiver Room (does some pumping of vinyl chloride).	6%
9	Area of scales in the Polymer #1 Receiver Room (pumping vinyl chloride).	20%
11	Inside a small analyzer room (checks the phenol content in samples of monomers).	6%
6	Area of #4 drier and kettle trap (attends the control panel for the still).	31%
-	Other duties outside.	25%
-	Lunch room.	12%
TOTAL		100%

Chemical Confidential Material Produced Pursuant
To Protective Order
Federal Reserve Bank, Case No. 20-4837
U.S. District Court, N.D.
Southern District of New York
Case No. 24 CV-0003 (JH)
Western District of New York

R&S 000449

In reporting the results of the continuous monitoring system as vinyl chloride the assumption has been made that vinyl chloride exists in the general atmosphere in much higher concentrations than does vinylidene chloride and that it is vinyl chloride which the operators encounter most of the time. Table IV shows the results of air samples collected at a few of the air sampling locations with subsequent analysis by a vapor phase chromatographic technique. This method of analysis provides a differentiation between the concentrations of vinyl chloride and vinylidene chloride. Vapor concentrations of vinyl chloride were found to be about six times as great as vinylidene chloride in the general atmosphere. In reporting analyzer data as vinyl chloride it is believed there would not be a hazard to health from vinylidene chloride providing the exposures to vinyl chloride are controlled to within safe levels.

Only Chemicals for Research Material Produced Pursuant
to Order of the
U.S. District Court, Eastern District of New York
Case No. 94-71036 (Sd)
United States of America
Western District of New York

Table IV

COMPARISON OF THE RATIO OF VINYL CHLORIDE TO VINYLIDENE CHLORIDE
GENERALLY EXISTING AT A FEW AIR SAMPLING LOCATIONS,
3/27/63, 9:00 A.M.

Air Sampling Location	Vapor Concentrations			
	Vinyl Chloride		Vinylidene Chloride	
	ppm	Ratio %	ppm	Ratio %
#1	21.0	88	3.0	12
#7	10.5	90.5	1.1	9.5
#9	6.2	74	2.2	26
#12	9.8	89	1.2	11
AVERAGE		<u>85.4</u>		<u>14.6</u>

R&S 000451

Dow Chemical Confidential Material Produced Pursuant
To Protective Order
Case No. 80-4837
U.S. District Court
Southern District of New York
Case No. 80-4837
Western District of New York

Western District of New York
last period from

R&S 000452

Date Original Confidential Material Produced Pursuant
to Executive Order 11652
Date Declassified Date File #80-4337
Exempt from Release
Columbia Broadcasting System Company
Case No. 94CV00363 (SM)
Western District of New York

R&S 000453

R&S 8 X 8 TO THE INCH 350-3L
 RUFFEL & TERRY CO.
 BOSTON, U.S.A.

TIME WEIGHTED AVERAGE CONCENTRATIONS PPM

CHART 1-A

AVERAGE WEEKLY TIME WEIGHTED EXPOSURES TO VINYL CHLORIDE
 FOR THE POLYMER #1 REACTOR OPERATORS OVER A SIX MONTH
 PERIOD 1/5/62 - 6/18/62

SIX MONTH AV

1ST SHIFT 27.26 PPM

2ND SHIFT 28.96 PPM

3RD SHIFT 30.27 PPM

DAY AV 28.83 PPM

DATA

2057

JANUARY

FEBRUARY

MARCH

APRIL

MAY

JUNE

R&S 000454

REPRODUCED BY R&S

CHART 1-B

AVERAGE WEEKLY TIME WEIGHTED EXPOSURES TO VINYL CHLORIDE
FOR THE POLYMER #1 REACTOR OPERATORS OVER A THREE MONTH
PERIOD 1/16/63 - 4/10/63

THREE MONTH AV.

1ST SHIFT 72.59 PPM

2ND SHIFT 85.47 PPM

3RD SHIFT 78.52 PPM

DAY AV. 79.09 PPM

K&E 825 TO THE INCH 359-3L
TIME WEIGHTED AVERAGE CONCENTRATIONS PPM

SEE CHART #1-C

Vertical axis label: K&E 825 TO THE INCH 359-3L

Vertical axis label: K&E 825 TO THE INCH 359-3L

R&S 000455

1/22 1/29 2/5 2/12 2/19 2/26 3/5 3/12 3/19 3/26 4/2 4/9

AVERAGE

CONCENTRATION

PP17

150

160

146

5/2

01/05

8

6

4

1.

Q H A R T - 1 - C

DATE/ TIME WEICARD AVERAGG CONTACTIVITY OF VINYL CHLORIDE ENCOUNTERED BY THE POLYMER AT

KETTLE HILL 1/30/67 - 2/5/63

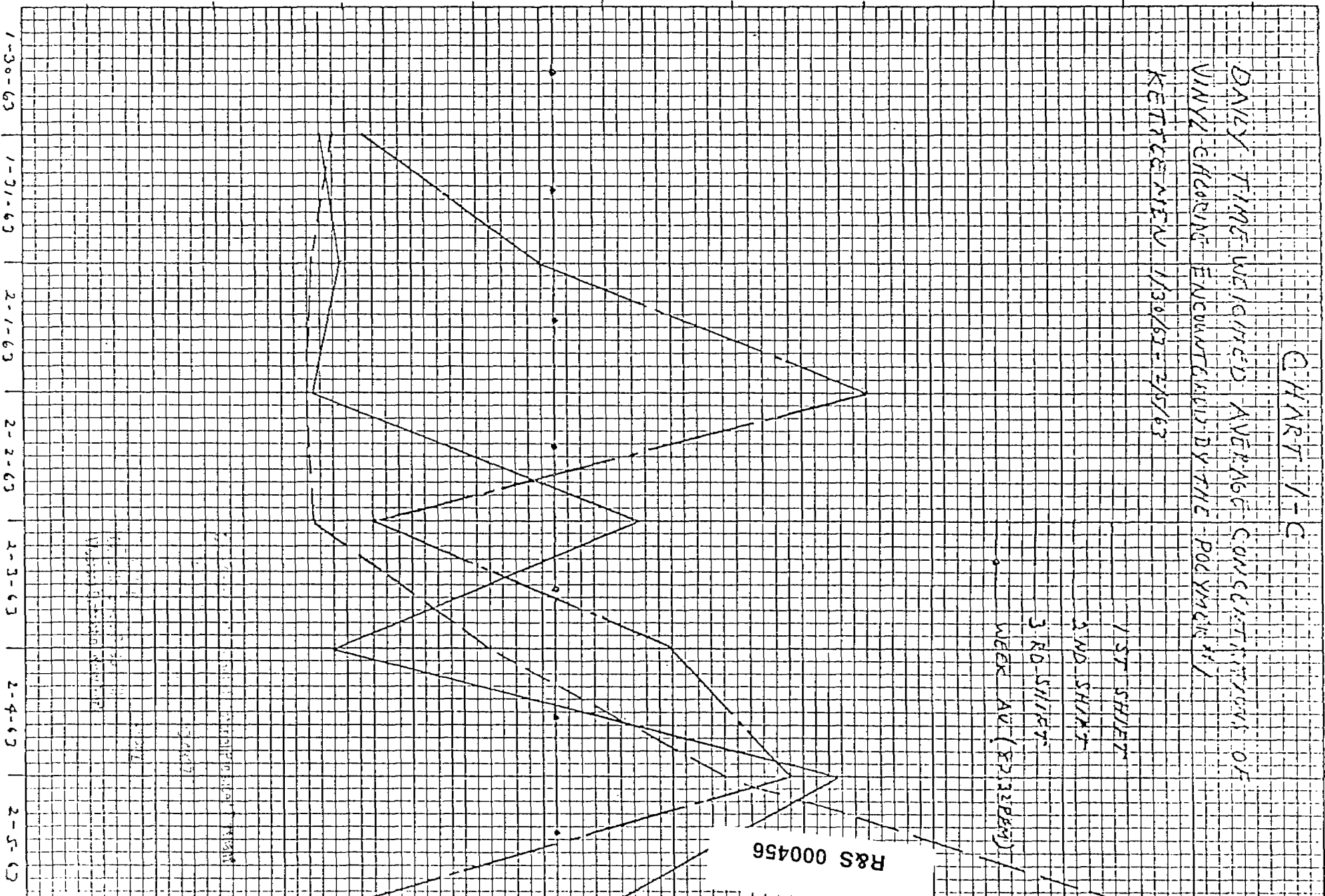
1575 H/E 2

5ND-SH17

3 RD-51157-

WE EX AU (87.32PM)

R&S 000456



The reason for the wide variation in the operator's exposures between the two environmental surveys was first considered to be due to an increase in production in 1963. This did not prove to be the case. Chart 2 shows the number of batches of Saran produced in the Polymer #1 and #2 sections and it can be seen, except for the month of January, 1963, there was considerable more Saran produced in 1962 than there was in 1963 for comparable months. It was true there was much more Saran produced in the Polymer #1 section than produced in the Polymer #2 section, however, the average exposures as vinyl chloride in 1962 were about equal for both the Polymer #1 and #2 reactor operators regardless of the wide differences in the production of Saran by the two sections (compare charts 1-A and 3-A). All in all, there does not appear to be a direct correlation between operator's vapor exposures and number of batches of Saran produced.

R&S 000457

Produced Pursuant
Case No. 60-4337
Chemical Company
Western District of New York

NUMBER BATCHES PER MONTH



R&S 000459

Charts 3-A and 3-B show the time-weighted weekly average exposures as vinyl chloride for the reactor operators (kettle men) of the Polymer #2 section during the two environmental study periods. Charts 4-A and 4-B show comparable time weighted exposures for the still operators of the Polymer #1 and #2 sections. The irregular pattern of the time-weighted exposures reveals that at times vapor concentrations were high, however, in averaging the exposures over a period of time it can be seen the amounts are well under a recently proposed safe limit of 50 ppm of vinyl chloride for daily repeated exposures. Exposures for the reactor operators of Polymer #2 did not increase in 1963 over 1962 whereas the exposures for the reactor operators of Polymer #1 did. Possibly the difference may be due to newer equipment, better room ventilation (larger operating areas), and less chance for faulty operating techniques because of the reduced production. While these are possible reasons for the lesser vapor exposures of the Polymer #2 operators they are by no means known causes of the lesser exposures.

Exposure to Chemical Material Produced Pursuant
to Federal Order
Case No. 93-4337
Southern California
Southwest Oil Company
Case No. 93-4337
Western District of New York

CHART 3-A

AVERAGE WEEKLY TIME WEIGHTED EXPOSURES TO VINYL CHLORIDE

FOR THE POLYMER #2 REACTOR OPERATORS OVER A SIX MONTH

PERIOD 1/5/62 - 6/18/62

SIX MATH AV.

✓ J L L S H Y E T

17.42 PPM

END SHIPT

20-27-74 PM

ORD 54757

2249 784

048 20

20.66 PPM

DATA

2057



R&S 000460

THREE MONTHS ON.

1 ST SIFT 13 48 PM

2ND SHIFT 16.44 PM

3RD SHAFET IS 30 PP

DAY, AUG 15, 30 PM.

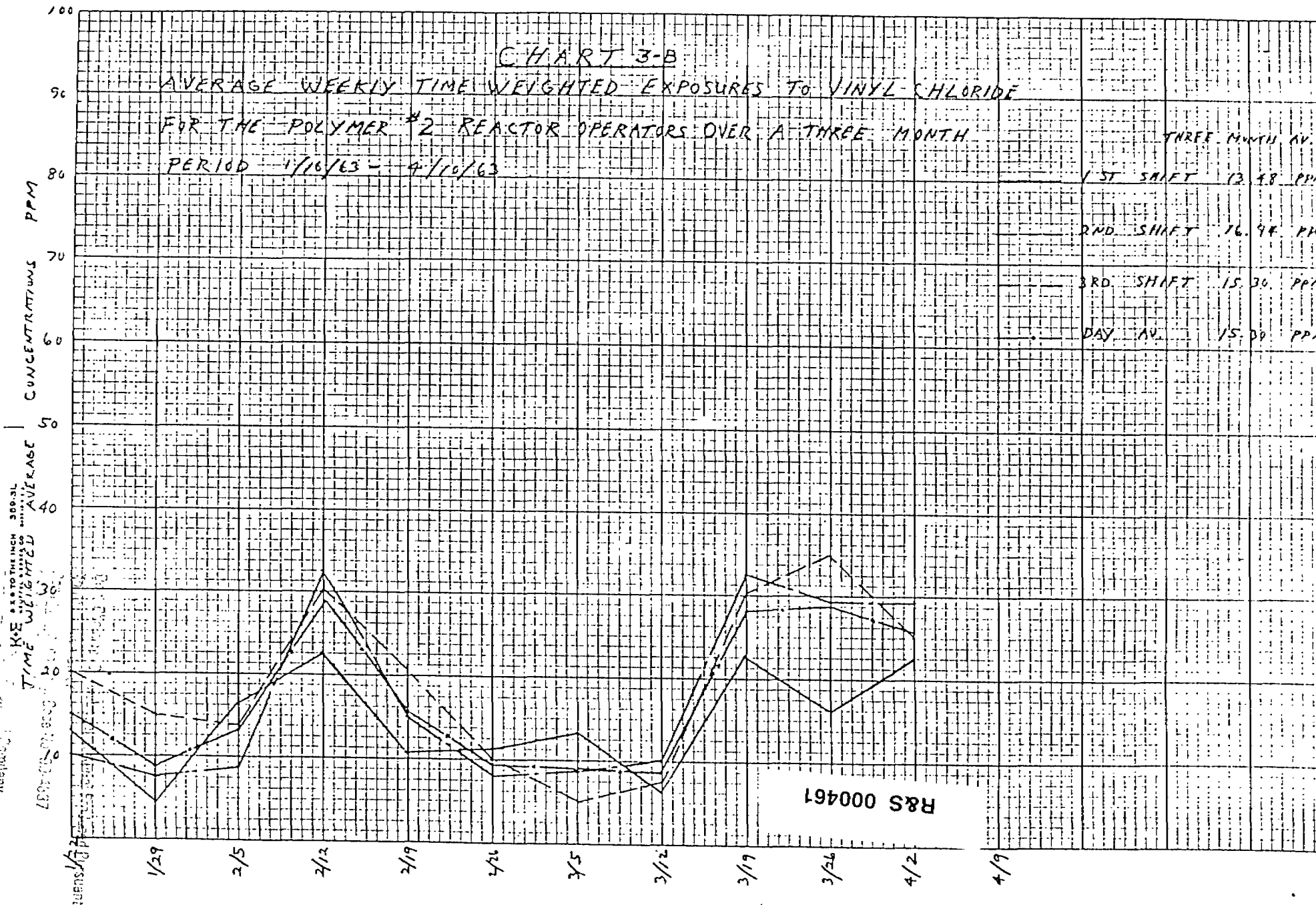


CHART 4-A

AVERAGE WEEKLY TIME WEIGHTED EXPOSURES TO VINYL CHLORIDE
FOR THE POLYMER #1 AND #2 STILL OPERATORS OVER A SIX MONTH

PERIOD 1/1/62 - 6/18/62

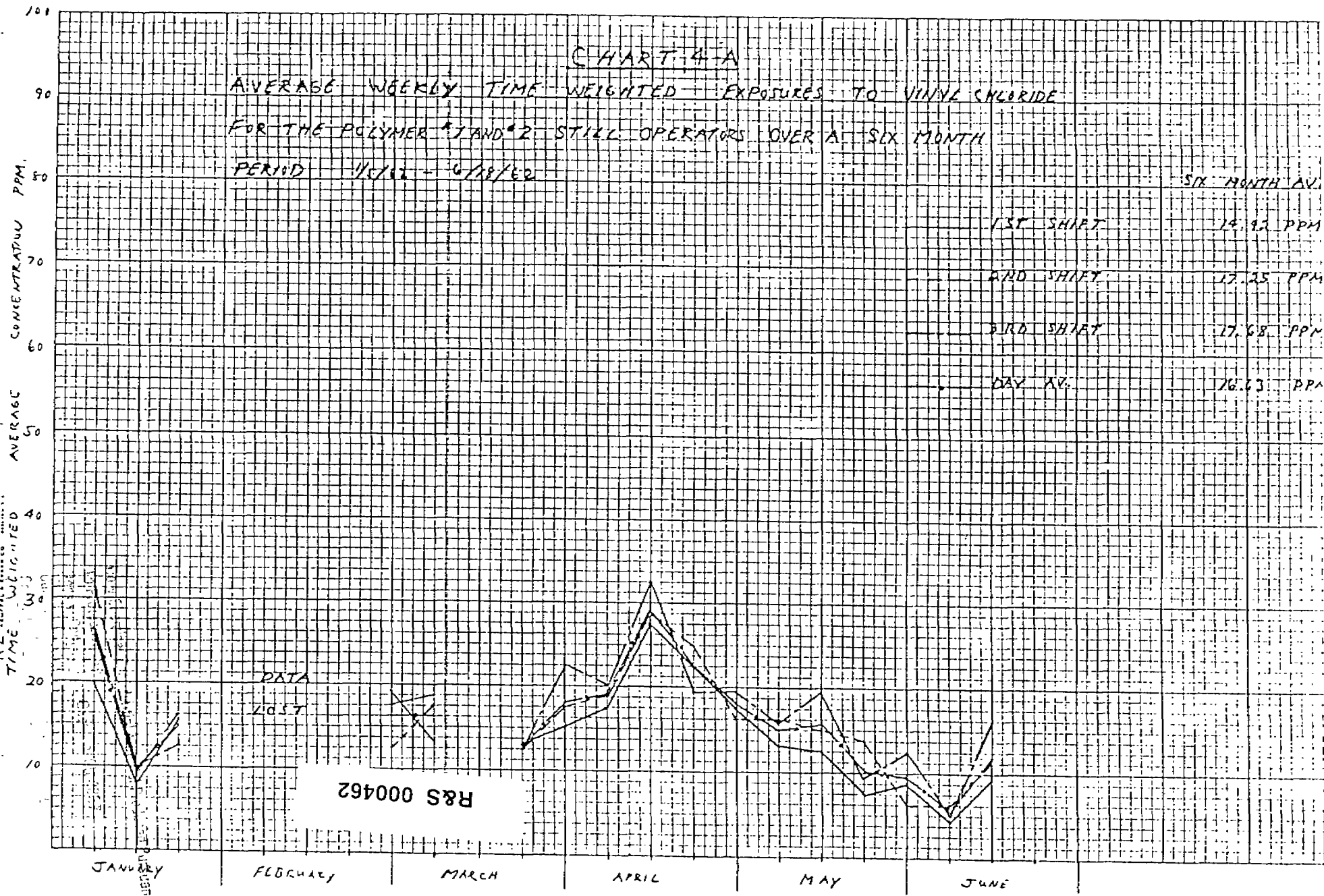


CHART 4-B

AVERAGE WEEKLY TIME WEIGHTED EXPOSURES TO VINYL CHLORIDE

FOR THE POLYMER #1 AND #2 STIAL OPERATORS OVER A THREE MONTH

PERIOD 1/16/63 - 4/10/63

THREE MONTH AV.

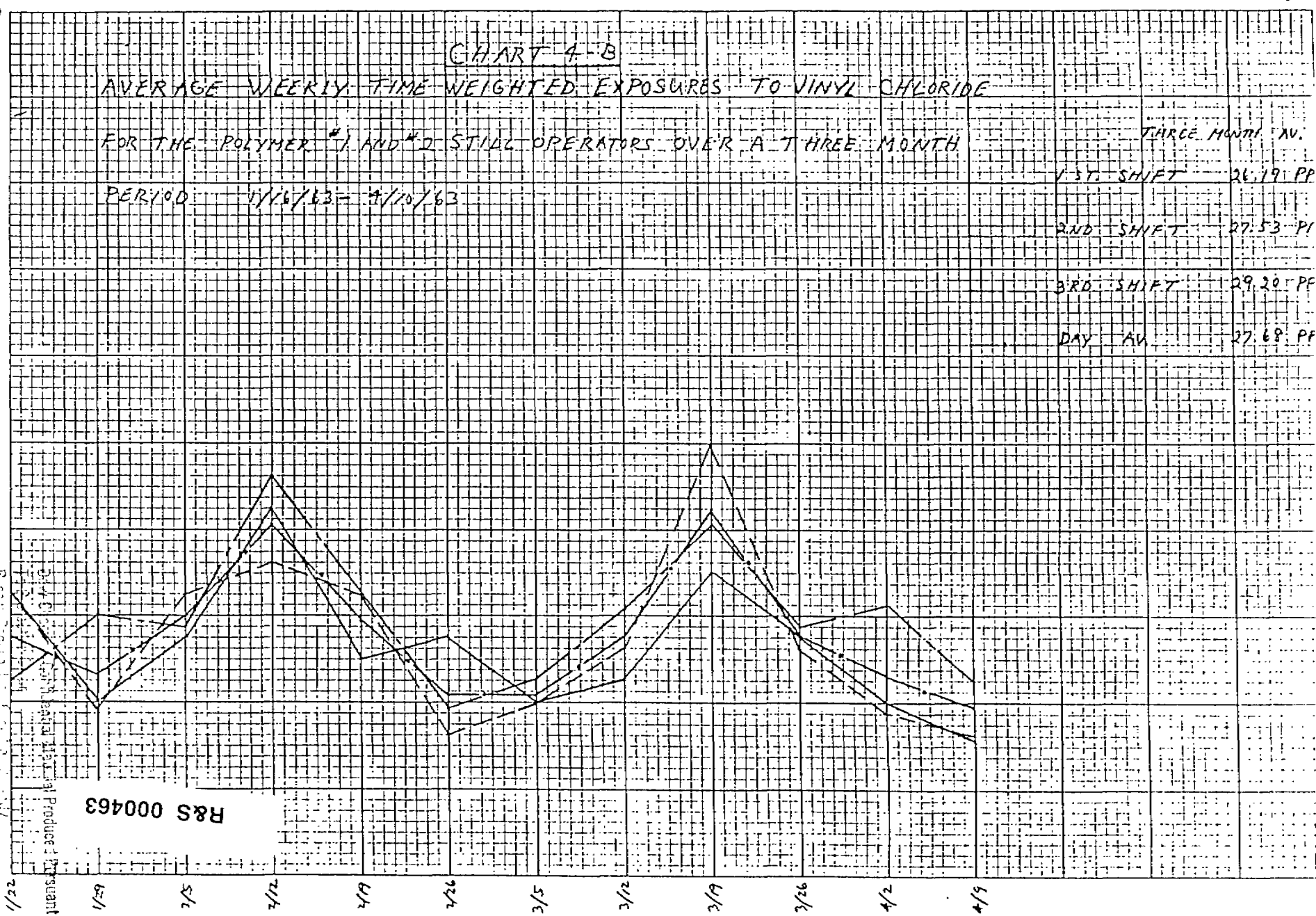
1ST SHIFT 26.19 PP

2ND SHIFT 27.53 PP

3RD SHIFT 29.20 PP

DAY AV 27.68 PP

PPM
AVERAGE CONCENTRATIONS
TIME WEIGHTED



R&S 000463

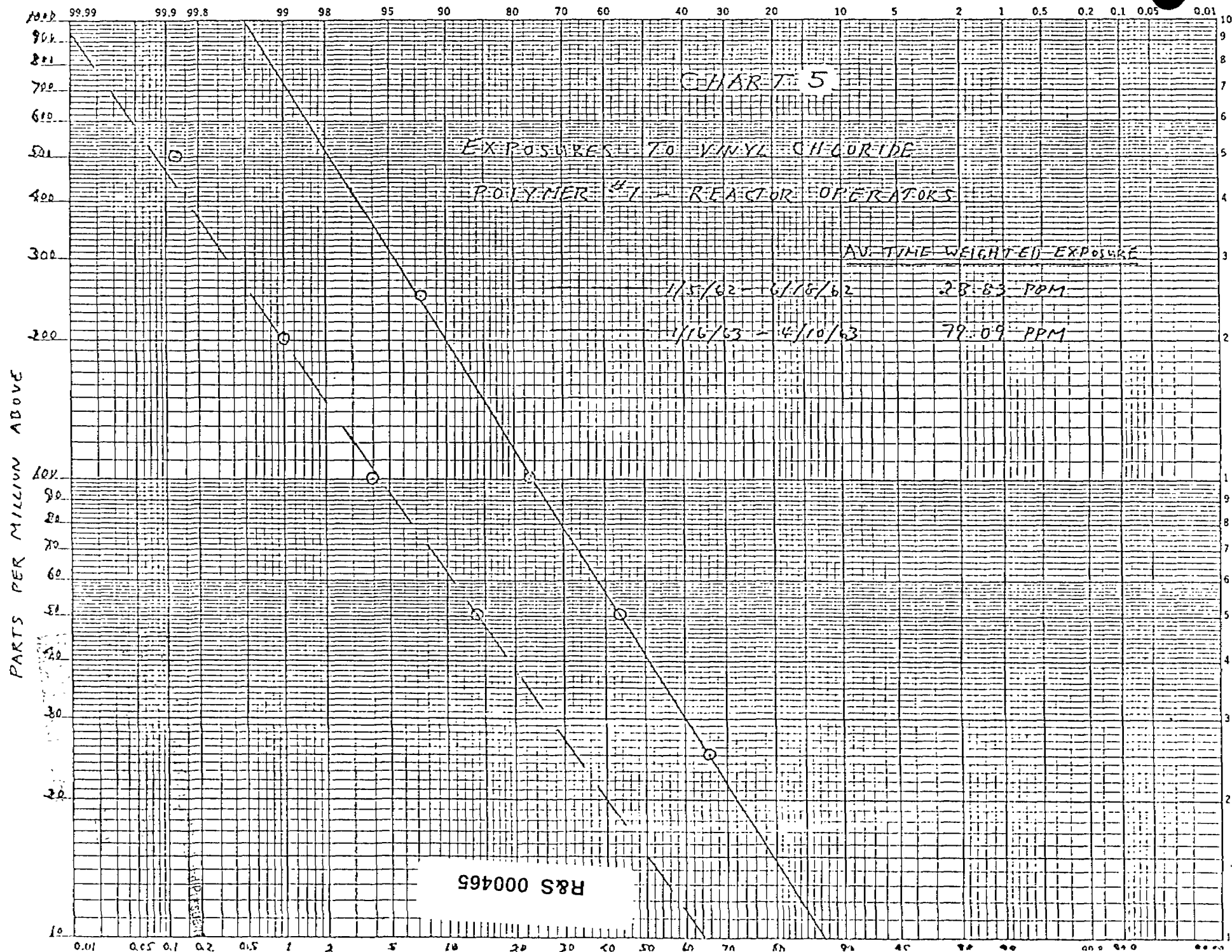
Can. Lab. 100-100
Wentworth, New York

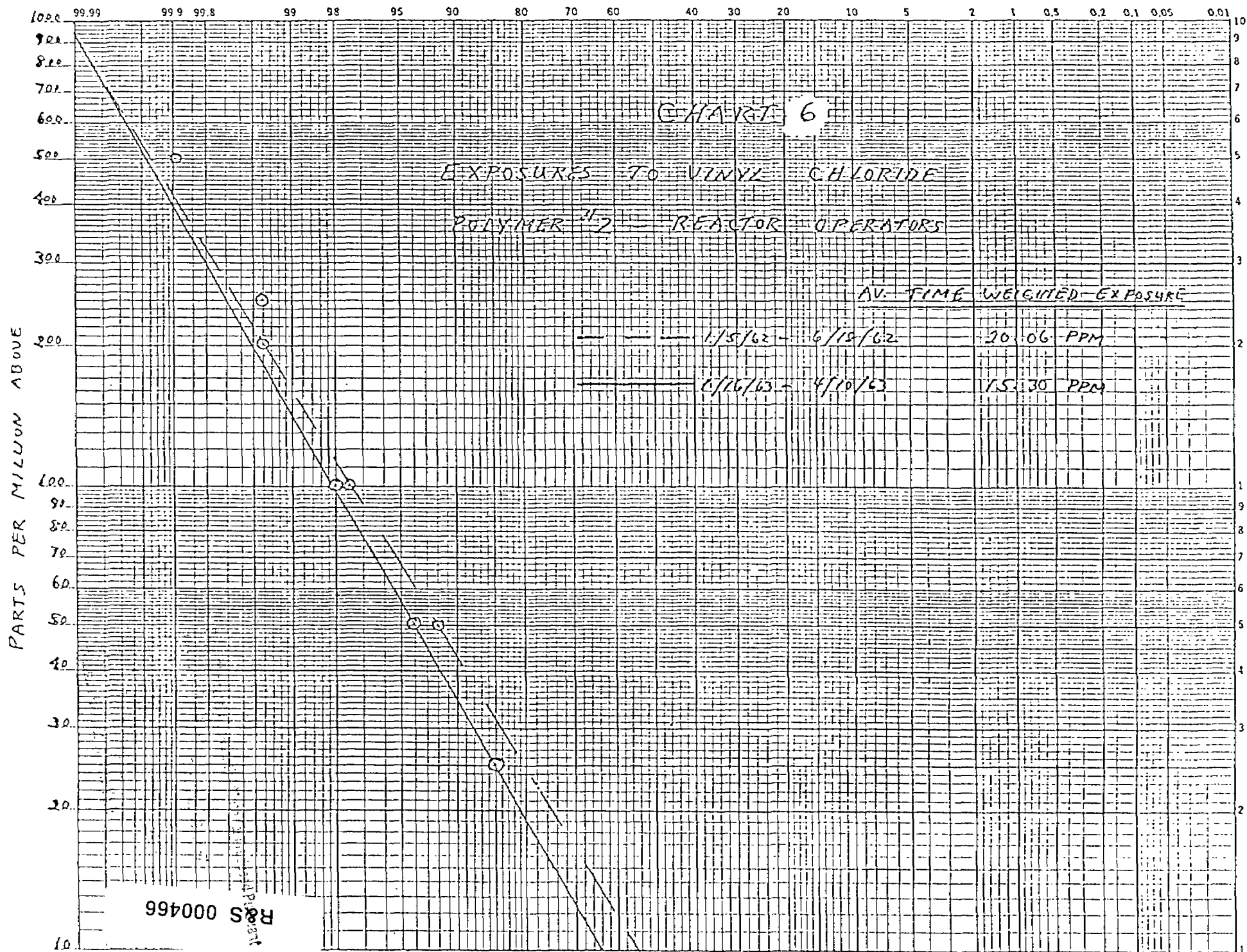
When the program for the computer was being devised it was thought a valuable interpretation of the data would be obtained if the percentage of time when the concentration of vinyl chloride and/or vinylidene chloride exceeded certain levels was recorded. Provisions were made to determine the percentage of time which the vapor concentrations as vinyl chloride exceeded 25, 50, 100, 200, 250 and 500 ppm.

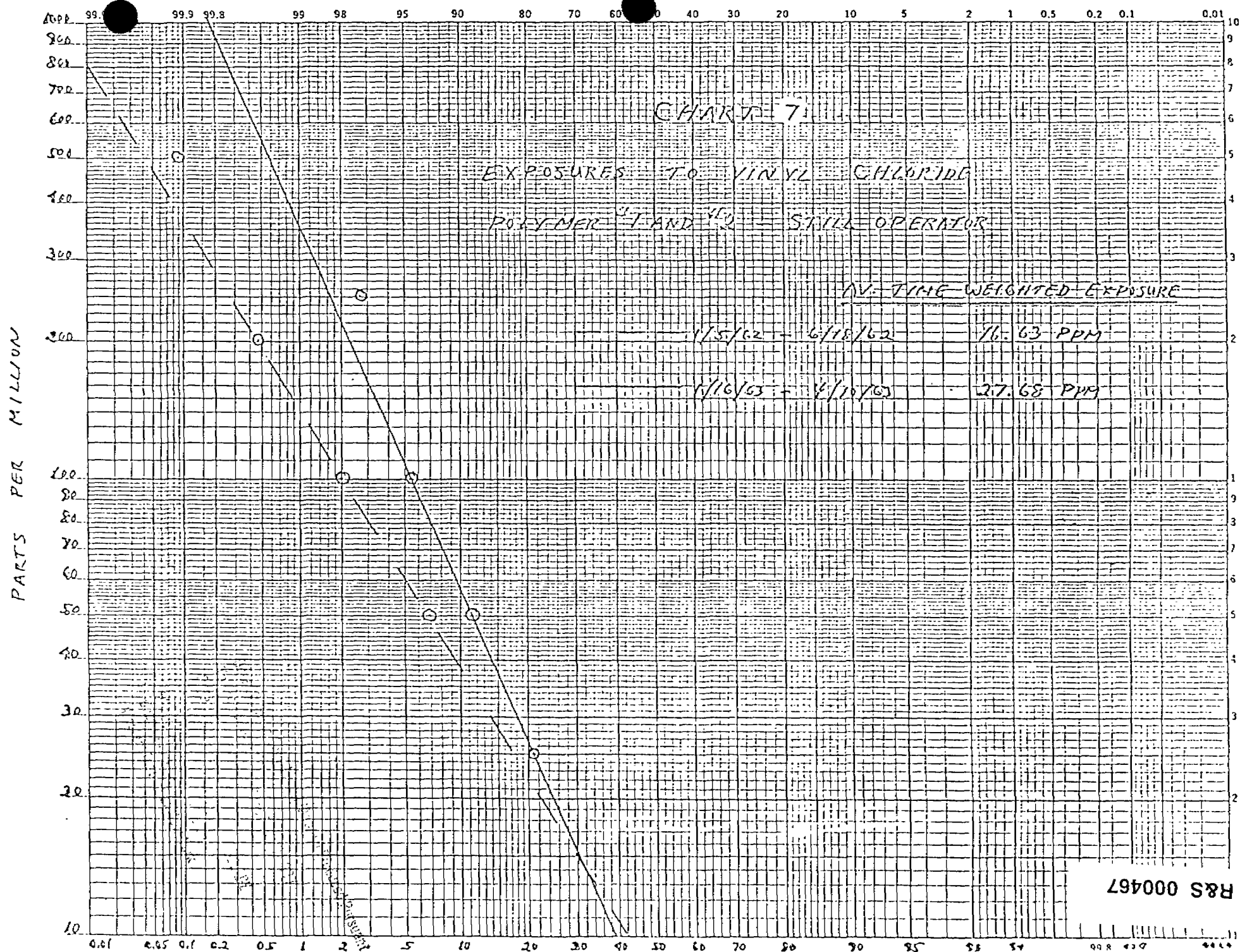
Charts 5, 6 and 7 are plots of the percentage of time the operator's weighted average exposures as vinyl chloride exceeded the indicated concentrations. This data reveals that all the operator's exposures to high concentrations of vapors are for very short periods of time. Except for the reactor operators of Polymer #1 in 1963, even exposures near the standard 50 ppm vinyl chloride represented no more than 10% of the operator's exposures. It is not likely that there has been a hazard to health for the reactor operators of Polymer #2 or the still operators from this sequence of vapor exposures.

However, if the reactor operators of Polymer #1 are permitted to continue to encounter vapor concentrations as of 1963 where 50% of the time the concentrations exceeded 50 ppm and 25% exceeded 100 ppm, a chronic hazard to health might well exist (see addendum to report).

Don't Change Confidential Material Produced Pursuant
To Executive Order 11652
R&S 000464, Serial 004837
100-442361
U.S. DEPARTMENT OF JUSTICE
Western District of New York







R&S 000467

RECOMMENDATIONS

In the interest of reducing the exposure of Polymer #1 kettle men to vapors of vinyl/vinylidene chloride provisions should be made to evaluate all possible sources of exposure. Daily observance of the halogenated hydrocarbon analyzer charts by supervision and operators will greatly aid in detecting leaks at an early stage and prevent exposures to high concentrations of vinyl/vinylidene chloride for extended periods of time. Operators should identify the source of exposure and indicate on the charts the corrective action taken. Other uses of continuous air analyzers have obtained improved operation and environmental control through strict adherence to this approach.

R&S 000468

Do not Destroy Confidential Material Produced Pursuant
To Protective Order
E-133 - Case No. 92-171, Case No. 92-4837
U.S. District Court
Southern District of New York
U.S. District of New York

ADDENDUM

Significance of the Exposures to Vinyl Chloride and/or Vinylidene Chloride

The relatively long lapse of time in reporting the results of the environmental surveys conducted in the Saran Plant in 1962 and 1963 has been due to an uncertainty concerning the actual degree of toxicity of vinyl chloride to the human liver and kidneys as a result of repeated exposures to low concentrations.

Until quite recently, all published data has indicated that vinyl chloride is primarily a central nervous system depressant, causing symptoms of dizziness and disorientation with little or no effect on the liver and kidneys. The present published Industrial Hygienic Standard for vinyl chloride is 500 ppm.

However, the toxicologists of our own Biochemical Research Laboratory, conducting studies of exposures to vinyl chloride and also to vinylidene chloride, report evidence of liver and kidney damage in animals from both materials. It is their feeling that for regular daily 7-8 hour exposures of humans the peak concentrations of vinyl chloride in the work environment should not exceed 100 ppm with a time-weighted average for all exposures not to exceed 50 ppm. Vinylidene chloride proved to be even more toxic to the liver and kidneys than vinyl chloride. Recommended limits are that peak concentrations of

R&S 000469

Western Union
New York, N.Y.
Produced Pursuant
to Federal Court Order
No. 80-4837
S. H. K. Company
New York, N.Y.
Western Union of New York

vinylidene chloride in the work environment should not exceed 50 ppm with a time-weighted average for all exposures not to exceed 25 ppm. Vinylidene chloride is considered to be very similar to carbon tetrachloride in its toxicity. The toxicological studies of vinylidene chloride have not been challenged, however, in 1963 about the time the environmental studies at the Saran Plant were completed, toxicologists at Yale University published the results of other studies of exposures to vinyl chloride on both animals and humans. Their contention was that the alterations in liver morphology observed by our laboratory were within a normal range and were not pathologic in character. They concluded that the Industrial Hygiene Standard for vinyl chloride should not be lowered but should remain at 500 ppm until more studies are conducted to prove differently.

Reporting of the results of the environmental surveys has been postponed in hopes that further clarification of the toxicity of vinyl chloride would be forthcoming. That hope was not well founded; consequently, an interpretation of the results of the environmental surveys is being made at the time in the light of the data available.

As stated in the report, the time-weighted exposures as vinyl chloride were compared with Dow-proposed limits for vinyl chloride for the following reasons:

- 1) Operators in the Saran Plant are actually exposed to a combination of vinyl chloride and vinylidene chloride.

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New Chemical Confidential Material Produced Pursuant
To Federal Order No. 99-4837
Dow Chemical Company
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Midland, Texas 79701
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New York

R&S 000470

2) An effect was definitely noted on the liver and kidneys of animals which were exposed to vinyl chloride as was also the case with vinylidene chloride in our laboratory.

3) The environmental study was comprehensive enough to present an accurate account of the operator's average time-weighted exposures.

4) There are several peak exposures to vinyl chloride and/or vinylidene chloride of very high concentrations "super-imposed" on a low base encountered by the operators. The true significance of these exposures is not known but should not be overlooked.

Dow Chemical Confidential Material Produced Pursuant
To Production Order
R-11, 215, 12, 13, Case No. 99-4837
Dow Chemical Company
1800 Market Street
New York, New York

R&S 000471

UNIT INDEX

An evaluation of exposures to vinyl/vinylidene chloride encountered by reactor and still operators of the Polymer #1 and #2 sections of the Saran Production Plant was conducted in January-June, 1962, and January-April, 1963, using a continuous vapor concentration monitoring system. Datex data recording equipment and a digital computer were utilized to conveniently evaluate the results. Time-weighted average exposures to vinyl/vinylidene chloride indicate a possible chronic hazard to health for the reactor operators (kettle men) of the Polymer #1 section. Improved operating techniques and periodic maintenance of equipment is need to keep exposures to within acceptable levels.

DISTRIBUTION

A. T. Look, Plastics Production, 433A Building
E. M. Haas, Saran Production, 262 Building
R. E. Onan, Saran Production, 262 Building
H. H. Gay, M.D., Medical Department, 607 Building
R. D. Stewart, M.D., Medical Research, 607 Building
A. W. Wilson, Safety Department, 401 Building
R. A. Brown, Safety Department, 401 Building

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Washington, D.C. 20540