

VINYL CHLORIDE-POLYVINYL CHLORIDE TOXICOLOGY

- 1930 1. Patty, F. A., et al, "Acute Response of Guinea Pigs to Vapors of New Commercial Organic Compounds", Public Health Reports, 45, 1963.
- 1937 2. Union Carbide Corporation established a Chemical Hygiene Fellowship under Dr. H. F. Smyth at Mellon Institute of Research, Pittsburgh, Pennsylvania.
- 1940-1944 3. Mellon Institute of Research conducted sixteen studies of skin sensitization by vinyl chloride resins and compounds.
- 1947 4. Smyth, H. F., Jr. and Weil, C. S., "Chronic Oral Toxicity to Rats of Vinyl Chloride-Vinyl Acetate Copolymer", Toxicology and Applied Pharmacology, 9, 501-504, 1966.
- The work started in 1944 involved feeding rats diets containing 1.5% and 12% of a vinyl chloride resin for two years and included two generations of reproductive studies. No effect attributable to the resin was found.
5. Animal Feeding Studies on Geon 202 by Harvard University for the B. F. Goodrich Company. (Geon 202 is a copolymer of vinyl chloride-vinylidene chloride.)
- The feeding of a diet containing five percent by weight of resin to laboratory rats for two years produced no toxic effects or retardation of growth.
- The feeding of a diet containing five percent by weight of resin to two dogs did not produce toxic effects or retardation of growth.
6. Oster, R. H., et al, "Narcosis with Vinyl Chloride", Anesthesiology, 8:359, 1947.
- 1949 7. Carr, J. et al, "Chemical Constitution of Hydrocarbons and Cardiac Automaticity", Journal of Pharmacology Exptl, Ther. 97, 1, (1949).

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- 1949 8. Tribukh, S. L., et al, Gigenia Sanit., 10:38.
Quoted by Marsteller, et al, Splenomegalic Liver Disease, Toxicity of Vinyl Chloride-Polyvinyl Chloride, New York Academy of Sciences, Vol. 246, 1975.
- 1955 9. Von Oettingen, W. F., "The Halogenated Hydrocarbons, Toxicity and Potential Dangers", United States Public Health Service Publication Number 414, Government Printing Office, Washington, D. C. (1955).
10. Oppenheimer, B. S., et al, "Further Studies of Polymers as Carcinogenic Agents in Animals", Cancer Research, 15, pp. 335-340, 1950.
- 1956 11. Smyth, H. F., Jr., "Improved Communications-Hygiene Standards for Daily Inhalation", American Industrial Hygiene Association Journal, p. 129, 17, 1956.
- 1960 12. Mastromatteo, E., et al, "Acute Inhalation Toxicity of Vinyl Chloride to Laboratory Animals", American Industrial Hygiene Association Journal, p. 394, 5, 1960.
Bulletin Hygiene, 36:244.
- 1961 13. Torkelson, T. R., et al, "The Toxicity of Vinyl Chloride as Determined by Repeated Exposure of Laboratory Animals", American Industrial Hygiene Association Journal, p. 354, 22, Number 5, 1961.
14. Oppenheimer, E. T., et al., "Observations on the Effect of Powdered Polymer in the Carcinogenic Process", Cancer Research, p. 132, 21, 1961.
- 1962 15. The American Congress of Governmental Industrial Hygienists set the worker exposure to vinyl chloride at 500 ppm for eight-hour TWA weighted average.
16. Lester, D., et al, "Effects of Single and Repeated Exposures of Humans and Rats to Vinyl Chloride", American Industrial Hygiene Association Meeting, Washington, D.C., May, 1962.

- 1963 17. The American Congress of Governmental Industrial Hygienists set the worker exposure to vinyl chloride at 500 ppm threshold limit value.
- 1966 18. The Manufacturing Chemists Association Occupational Health Committee met to discuss reported acroosteolysis at B. F. Goodrich, Company plants in October 6, 1966.
- 1967 19. The Manufacturing Chemists Association sponsored a study of the epidemiology of acroosteolysis in the United States.
20. Wilson, R. H., et al, "Occupational Acroosteolysis", Journal of American Medical Association, Vol. 21, No. 8, 1967.
- 1968 21. Mutchler, J. E., et al, "Report on the Relation of Exposure to State of Health of Dow Chemical Workers", Gordon Conference, Tilton, New Hampshire, 8-1968.
- 1969 22. Popow, Jerzy, "Effect of Polyvinyl Chloride (PVC) Dust on the Respiratory System of the Rat", Roczniki Akademii Medycznej im Juliana Marchlewskiego w Białymstoku, Supplement 24, p. 5, Vol. 48, 1969.
- (Rat exposure 92% of PVC dust particles less than five microns.)
23. Baretta, E. D., et al, "Monitoring Exposures to Vinyl Chloride Vapor: Breath Analysis and Continuous Air Sampling", American Industrial Hygiene Association Journal, p. 537, Vol. 30, 1969.
24. "Epidemiological Investigation of the Polyvinyl Chloride Industry in Reference to Occupational Acroosteolysis", The Institute of Industrial Health, The University of Michigan, February, 1969.
- 1970 25. Viola, P. L., "Cancerogenic Effect of Vinyl Chloride", Regina Elena Institute for Cancer Research, University of Perugia, Tenth International Cancer Congress, Houston, Texas, May 22, 1970.

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1970

Viola, P. L. (continued)

26. "Pathology of Vinyl Chloride", Medicina del Lavoro, Vol. 61, pp. 174-179, March, 1970.
27. "The Vinyl Chloride Disease", Publication not identified, Summer, 1970.
28. "Oncogenic Response of Rat Skin, Lungs and Bones to Vinyl Chloride", Cancer Research, pp. 516-522, Vol. 31, 1971.

1971

29. Szende, C. K., et al, "Pneumoconiosis Developing After Inhalations of Polyvinyl Chloride", Orv. Hetil. 112:85-6, January 10, 1971.

(This is a study of one case of pneumoconiosis where the authors raise the assumption that aspiration of PVC dust may lead to pneumoconiosis. Individual particles were oval or polygonal in shape and 15-25 microns in diameter.)

30. The Manufacturing Chemists Association Occupational Health Committee met with Dr. Viola May 5 and 6, 1971 to discuss the work reported.
31. On October 27, 1971 the MCA Occupational Health Committee recommended that a study of chronic inhalation toxicology be undertaken by industry.
32. On November 16, 1971 an Ad Hoc Planning Group for Vinyl Chloride Research was formed with R. N. Wheeler, Jr. of Union Carbide Corporation Chairman.
33. On December 14, 1971 the Ad Hoc Planning Group met in Washington, D. C. and adopted a basic research plan of:
 1. Chronic Inhalation Toxicity Study at three levels with rats, mice and hamsters.
 2. Vinyl chloride metabolism study.
 3. An Epidemiological Study of PVC Industry Mortality

The program would cost approximately \$350,000 for over a three- to four-year period.

(Maltoni at the end of 1970 planned a project to clarify the type and degree of carcinogenic risk from vinyl chloride sponsored by Montedison).

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- 1972 34. Manufacturing Chemists Association requests for sponsorship of the vinyl chloride research project produced subscription of \$165,000. The Ad Hoc Planning Group recommended starting the chronic inhalation toxicity study and delaying the remainder of the program until money was available. The Ad Hoc Group disbanded and was replaced by the MCA Technical Task Force for Vinyl Chloride Research under Dr. T. R. Torkelson of Dow.
35. Kramer, C. G., et al, "The Correlation of Clinical and Environmental Measurements for Workers Exposed to Vinyl Chloride", American Industrial Hygiene Journal, January, 1972.
36. The American Congress of Governmental Industrial Hygienists recommended that the TLV for vinyl chloride be reduced to 200 ppm for workers.
37. Chemical Safety Data Sheet SD-56 Vinyl Chloride Manufacturing Chemists Association revised, 1972.
- 1973 38. The Manufacturing Chemists Association contracted with Industrial Biotest Laboratory to carry out the long-term chronic inhalation study of vinyl chloride. The project was delayed due to relocation of the laboratory and due to unsatisfactory laboratory conditions.
39. The Manufacturing Chemists Association contracted with Tabershaw Cooper Associates, Berkeley, California to do a retrogressive epidemiology study of the workers in the VCM and PVC industry.
40. The MCA also contracted with Dow Chemical to study the metabolism of vinyl chloride in animals on a best efforts basis for one year.
41. Informal reports in confidence were received from Dr. C. Maltipni via Imperial Chemical Industries that rats exposed to 250 ppm of vinyl chloride were showing evidence of tumors. These results, as well as the Manufacturing Chemists Association research program, were discussed with Dr. Marcus Key and associates of NIOSH in mid year by representatives of MCA, Dow, Ethyl, Union Carbide Corporation and Imperial Chemical Industries.
42. Manufacturing Chemists Association reported to NIOSH, EPA and OSHA that mice exposed in the Industrial Biotest Laboratory study were showing evidence of angiosarcoma.

- 1974 43. The B. F. Goodrich Company reported on January 23, 1974 five workers at their Louisville, Kentucky plant had died of angiosarcoma.
44. NIOSH convened a group of labor, industry and governmental consultants to consider the problem. Union Carbide Corporation was represented by R. N. Wheeler, Jr. The group was unable to agree on a common program and was disbanded after two meetings.
45. Recommended Standard for Occupational Exposure to Vinyl Chloride, National Institute for Occupational Safety and Health, United States Department of Health, Education and Welfare, 1974.
46. OSHA promulgated an Emergency Temporary Standard for Exposure to Vinyl Chloride. Worker exposure was to be limited to 50 ppm ceiling vinyl chloride.
47. Richardson, H. L., "Angiosarcoma of the Human Liver", United States Environmental Protection Agency, April 17, 1974.
48. Occupational Safety and Health Administration Exposure to Vinyl Chloride, United States Department of Labor, (29 CFR 1910.1017) October 21, 1974.
49. Proposed Regulation Vinyl Chloride Final Environmental Impact Statement, Occupational Safety and Health Administration, United States Department of Labor, 1974.
- 1975 50. OSHA promulgated a Permanent Standard for Vinyl Chloride Exposure with permissible exposure limited to one ppm eight-hour TWA and five ppm ceiling value.
51. "Biological Reactivity of PVC Dust", Nature, Vol. 56, August 21, 1975.
52. "PVC Dust Fells Factory Mice Suggesting New Work Hazard", New Scientist, June, 1975.
53. "Epidemiological Study of Vinyl Chloride Workers", Tabershaw/Cooper Associates, Inc., 2180 Milvia Street, Berkeley, California 94704, May 3, 1974.

- 1975 54. "Vinyl Chloride, Code of Practice for Health Precautions",
Health and Safety Executive, London, 1975.
55. "VC/PVC: Berspiel einer Problemlosung, Herausgeber:
Verban Kunststoffherzeugende Industrie e.v. Frankfurt,
Main, 1975.
56. Scientific and Technical Assessment Report on Vinyl Chloride
and Polyvinyl Chloride, United States Environmental Protec-
tion Agency, 1975.
57. Standard Support and Environmental Impact Statement, Pro-
mulgated Emission Standard for Vinyl Chloride, United States
Environmental Protection Agency, 1975.
58. Adams, W.G.F. and Purchase I.F.H., "Is PVC Dust A Hazard?",
Unpublished Communication, Imperial Chemical Industries, Ltd.
Welwyn Garden City, Hertfordshire, England, July 23, 1975.
59. Lynch, A. L., "Evaluation of Ambient Air Quality by Personnel
Monitoring", pp. 141-145, C.R.C. Press, Inc., 1975.
60. Kuzmack, A. and McGaughy, R., "Quantitative Risk Assessment
for Community Exposure to Vinyl Chloride", United States
Environmental Protection Agency, 1975.
61. Proposed Standard for Vinyl Chloride, United States Environ-
mental Protection Agency, Society of the Plastics Industry
Comments, New York, 1975.
- 1976 62. Standard Support and Environmental Impact Statement, Emission
Standard for Vinyl Chloride, Volume II, United States Environ-
mental Protection Agency, 1976.
63. Report on a Mortality Study Covering Employees of PVC
Fabricators, Organization Resources Counselors, Inc., 1625
I Street, N. W., Washington, D. C. 20006, February, 1976.
64. Pigott, G. H., "In Vitro, Studies of a Range of Formulations
of PVC", American Chemical Society, New York, New York
Meeting, April 4, 1976.

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- 1976 65. Infante, P. F., et al, "Carcinogenic, Mutagenic and Teratogenic Risks Associated with Vinyl Chloride", Mutation Research, pp. 131-142, Vol. 41, 1976.
66. Wheeler, R. N., Jr., "Specialty Vinyl Chloride Resin Processes, Effects of Governmental Regulations", American Chemical Society, San Francisco, California Meeting, September, 1976.
67. Epidemiologic Study of Vinyl Chloride Workers Employed by Union Carbide Corporation, South Charleston, Plant, Equitable Environmental Health, Inc., 2180 Milvia Street, Berkeley, California 94704, December, 1976.
- 1977 68. Fox, A. J., et al, "Mortality Experience of Workers Exposed to Vinyl Chloride Monomer in the Manufacture of Polyvinyl Chloride in Great Britain", British Journal of Industrial Medicine, pp. 1-10, Vol. 34, 1977.
69. Baxter, P. J., et al, "Angiosarcoma of the Liver in Great Britain 1963-1973", British Medical Journal, pp. 919-921, Vol. 2, 1977.
70. Falk, Henry, et al, "A Cross-Sectional Epidemiologic Survey of Vinyl Chloride Workers", United States Department of Health, Education and Welfare, National Institute for Occupational Safety and Health, Cincinnati, Ohio, April, 1977.
71. Gehring, P. J., et al, "Resolution of Dose-Response Toxicity Data for Chemicals Requiring Metabolic Activation: Example-Vinyl Chloride", Dow Chemical U.S.A., Midland, Michigan 48640, July 12, 1977.
72. MacMahon, Brian, M.D., "Vinyl Chloride and Human Reproduction" The Society of the Plastics Industry, Vinyl Chloride-Polyvinyl Chloride Safety Group, August 15, 1977.
73. Downs, T. D., et al, "Vinyl Chloride, Birth Defects and Fetal Wastage, A Critical Review", The Society of the Plastics Industry, September 16, 1977.
74. Scamehorn, J. F. and Yang, Kang, "Diffusion of Vinyl Chloride in Polyvinyl Chloride Below the Glass Transition Temperature", American Institute of Chemical Engineers, New York, New York Meeting, November, 1977.

1978 75.Epidemiological Study of Vinyl Chloride Workers, Final
Report, Manufacturing Chemists Association, Washington,
D. C., February, 1978.

76.Chemical Safety Data Sheet SD-56 Vinyl Chloride, Manufactur-
ing Chemists Association Revised, February, 1978.

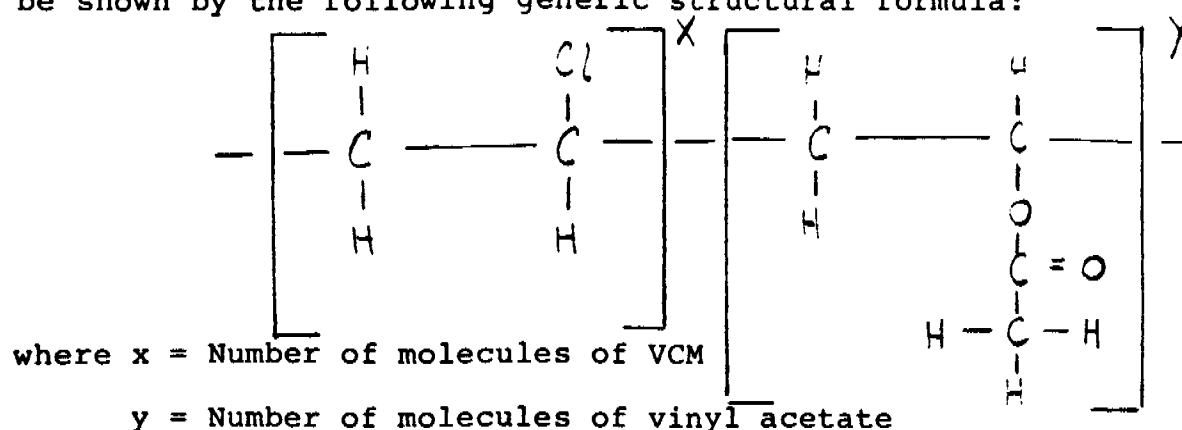
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Rider 7

PVC has no precise chemical formula and can best be shown by the following generic structural formula:



X may vary between 160 and 500 depending on the molecular weight of the product PVC and its comonomer, if any.

y is 0 for PVC homopolymer and up to possibly 20 for PVC copolymer

PVC may be known as polyvinyl chloride, vinyl chloride resin, vinyl chloride copolymer resin, or vinyl chloride homopolymer resin.

VCM, known as vinyl chloride or vinyl chloride monomer, is a precise chemical compound having the following structural formula:



Dates of initiation of manufacture are shown in answer to Interrogatory 5.

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Rider to Interrogatory 31(a)

<u>Year</u>	<u>Received</u>
1962	18.2 MM Lbs.
1963	57.0 MM Lbs.
1964	73.0 MM Lbs.
1965	67.3 MM Lbs.
1966	73.2 MM Lbs.
1967	55.2 MM Lbs.
1968	70.1 MM Lbs.
1969	74.0 MM Lbs.
1970	77.0 MM Lbs.
1971	70.1 MM Lbs.
1972	65.6 MM Lbs.
1973	53.0 MM Lbs.
1974	44.7 MM Lbs.
1975	13.4 MM Lbs.

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Rider 51

(a) The synthesis of vinyl chloride polymers was studied and reported in the literature by Baumann in 1872 and Ostromysslenskii in 1912. The synthesis of vinyl chloride and polyvinyl chloride by Union Carbide in approximately 1930 led to the development of commercial processes for their manufacture.

Problems that were solved by Union Carbide involved ~~the production of a very pure grade of vinyl chlori~~ of acetylides, preparation and use of organic catalysts, selection of a polymerization medium, of the polymer produced, stabilization of the manufacture of useful articles.

Hazards encountered in synthesis were explosion of metal acetylides, explosion of organic peroxide catalysts, flammability of organic gases and liquids, uncontrollable polymerizations, and acute toxicity of chlorinated hydrocarbons.

(b) Toxicity to the user was limited to evolution of hydrogen chloride gas by heating the polymer and skin irritation caused by compounds added to the resin by other fabricators to soften and stabilize the polymer.

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RIDER 56

Reliable methods of determining ppmw levels in resin were not developed until 1971 and were not widely used until 1974. Analytical results from different methods of analysis vary significantly even today i.e., Union Carbide's method of analysis yields higher results than that used by EPA.

Since analytical results are available only from 1974 onward and there is no resin lot identification for materials shipped to OTD/ATC no specific data can be supplied.

However, based on information and belief, the Union Carbide resins shipped to OTD/ATC contained the following amounts of unconverted vinyl chloride when produced.

Solution Process PVC resin	1 ppmw
Nonsolvent Process PVC resin	5-15 ppmw
Suspension Process PVC homopolymer resin	200-1000 ppmw
Suspension Process PVC copolymer resin	500-2000 ppmw

Vinyl chloride in PVC resin tends to escape to the ambient air. Therefore, resin arriving at OTD/ATC contained about 1/3 less VCM than the levels listed above and, when the resin was actually bagged at the OTD/ATC facility, the concentration of VCM (~~in the atmosphere~~) was very low.

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Rider 65

Potential hazards to persons exposed to air borne PVC arise from particles small enough to be respirable i.e., carried into the lung alveoli. The literature indicates that particles 10 microns or less in diameter can cause pneumoconiosis. If these respired particles contained free vinyl chloride monomer, it could be directly absorbed by the blood stream.

Measurements of Union Carbide resin particles indicate the following:

<u>Process</u>	<u>Percent 10 micron or less particles</u>
UCC Bulk Process Resin	0.4%
UCC Solution Process Resin	nil
UCC Suspension Process Resin	
QSAN-7	nil
VSJE	0.004%
UCC Dispersion Process Resin	99%

Dispersion Process Resin was not shipped to OTD/ATC.

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RIDER TO INTERROGATORY 71

In 1962 the American Congress of Governmental Industrial Hygienists (ACGIH) recommended that vinyl chloride exposure for workmen not exceed 500 ppm for an eight-hour time weighted average. The limit was set at concentrations believed to cause no adverse effect with repeated exposure.

In 1963 the ACGIH changed its recommendation to a 500 ppm threshold limit value.

On October 18, 1972, the Occupational Safety and Health Administration set the vinyl chloride exposure limit at a ceiling value of 500 ppm (1300 mg/m³).

In 1972 the ACGIH lowered its recommended vinyl chloride exposure limit to 200 ppm TLV. OSHA made no change in its standard.

On April 5, 1974, OSHA set its temporary Vinyl Chloride Standard limit at 50 ppm ceiling.

In April, 1975, an OSHA standard became effective, lowering the vinyl chloride exposure limits to 1 ppm maximum for an eight-hour time weighted average or 5 ppm maximum for any period not exceeding fifteen minutes.

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