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REV 8(E)

VCM-Exposure Standards. Too Tough Too Soon?

After virtually ignoring industry's findings on cancer risk for a decade, the U. S. government is now calling for zero-detectable ambient levels of vinyl chloride monomer (VCM) in plants that make or use it. At hearings this week, some clashes are expected as industry tells why it thinks the timetable should be extended.

Hearings begin tomorrow—June 25th—in Washington on just what level of exposure to vinyl chloride monomer (VCM) can be tolerated by workers without seriously endangering their health. Once again, and ironically in this instance, a clash between government agencies and industry seems inevitable.

The Occupational Safety and Health Administration (OSHA) proposes to set a standard for employee exposure at "zero," as determined by a sampling and analytical method capable of detecting vinyl chloride in concentrations of 1 ppm (with an accuracy of ±0.5 ppm).

OK, But . . .—VCM manufacturers are not basically opposed to reducing exposure levels as much as possible—for example, B. F. Goodrich Chemical Co. (the U. S.'s largest vinyl chloride producer) now operates at levels of about 15 ppm in its polymer plant, and even lower in its monomer facility. What bothers manufacturers is having to achieve, in a telescoped time-period "no detectable level of exposure."

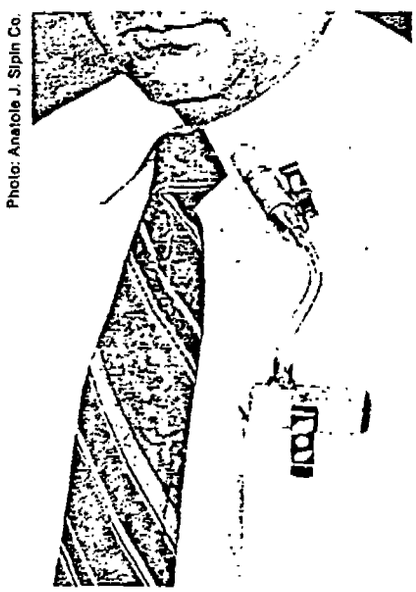

Photo: Anatole J. Sipin Co.

DEVICE measures VCM exposure by drawing air through sorbent tube.

As a Goodrich spokesman explains, "The situation we're facing with vinyl chloride exposure levels is not dissimilar to the zero pollution legislation for controlling water pollution—the final last percentage points are achievable only at enormously high costs."

The irony of this particular situation is that producers of vinyl chloride voluntarily alerted the government of the chemical's involvement in several deaths from liver cancer (angiosarcoma).

In fact, over 13 years ago Dow Chemical Co. reported that longterm VCM exposures of animals to 100 ppm VCM for 4½ to 6 mo. (at the equivalent of "normal working hours") resulted in slight liver damage. At that time, Dow recommended that exposure levels be reduced to 50 ppm, though the government's maximum allowable concentration was 500 ppm. The Dow recommendation was not accepted by the American Conference of Governmental Industrial Hygienists (ACGIH). In 1962, on the basis of work done at Yale University, ACGIH concluded that 500 ppm offered an adequate safety margin for human exposure to VCM, and published 500 ppm as the recommended standard. That same level was also accepted by OSHA as a national standard in 1971.

However, beginning in the mid-1960s, the Manufacturing Chemists Assn. funded an investigation of the possible health dangers involved in VCM manufacture. In mid-1972, MCA established technical liaison with European researchers who were also investigating the safe-exposure limits of VCM.

One decision by MCA arising from this agreement was to initiate an epidemiological study of VCM/PVC (polyvinyl chloride) workers in the U. S. And in early 1973, MCA signed a contract with Industrial Bio-Test Laboratories, Inc., (Northbrook, Ill.).

In late June 1973, MCA requested a meeting with the National Institute for Occupational Safety and Health; this was arranged for July 17, 1973. A summary of the published toxicity data on vinyl chloride, and other pertinent information, was presented to NIOSH at that time. A physician representing the European researchers reported at the meeting on studies in Europe in which tumors were observed in rats at exposure levels as low as 250 ppm.

Six months later, in January 1974, B. F. Goodrich Chemical Co. informed NIOSH that the deaths of several of its employees from angiosarcoma might have been occupationally related. In the succeeding months, similar reports were made to NIOSH of possibly job-related liver angiosarcoma by Union Carbide Corp., Goodyear Tire & Rubber Co. and Firestone Plastics Co.

In early April, OSHA acted and issued an Emergency Temporary Standard that reduced exposure levels from 500 ppm to 50 ppm, with the understanding that this new standard was to be in effect only until October while the whole question of VCM exposure safety levels was explored more closely.

Timetable Too Fast?—Despite what seems to be a long history of self-investigation and concern by the vinyl chloride industry, this week's scheduled hearings in Washington, are expected to spark some clashes. The industry is deeply concerned about the possible economic impact

of a "no detectable level" being established immediately.

In an effort to assess what the costs might be, the Soc. of the Plastics Industry, which is expected to participate in the hearings, has hired Arthur D. Little, Inc., the Cambridge, Mass., consulting firm, to prepare an economic impact survey.

Even the unions concur that economic hardships for workers could result from the proposed standard. However, as Anthony Mazzocchi, legislative director of the Oil, Chemical and Atomic Workers Union (which represents about 1,200 VCM/PVC workers) notes, "The men at Niagara Falls [where Goodyear has a plant] are caught. They're in a dilemma. What's their option? Work and eat today so they can die 20 years from now?" (Goodrich says the morale of its workers is good—men are still applying for jobs on its vinyl chloride line.)

What's Being Done—Simply stated, there are two major areas of concern in a VCM plant—ambient air containing vinyl chloride monomer particles, and the need to periodically enter the reactor vessels for cleaning. Research has indicated that the workers who clean the polymerization reactors by scraping are exposed to VCM concentrations of 600 to 1,000 ppm at hand level.

One monitoring device being looked at with interest is a personal sampling pump, manufactured by Anatole J. Sipin Co. (Although area-monitoring instruments have the advantage of immediate detection, they may not measure exact working conditions.) The Sipin device continuously draws an air sample from a worker's breathing zone through a sorbent tube over an 8-hr working an April of the organic materials breathed by a worker. The personal sample pump was looked at with interest by some Cincinnati-based NIOSH personnel at a meeting on monitoring for VCM, held in Houston.

As for reactor cleaning, GAF Corp. has developed a system whereby a solvent, trademarked M-Pyrol (*n*-methyl-2-pyrrolidone), is pumped through the heating unit and sprayed into the reactor to be cleaned. When about one-quarter full, the reactor is shut off and the solvent recirculated. The heavy spray of hot solvent absorbs the vinyl chloride monomer and, at the same time, dissolves the PVC residue.

Although PVC itself is considered an unusually inert material, residual monomer can be entrapped within the pores of the polymer. Up to now, the industry has not made it a practice to strip the residual monomer from the polymer. However, work is now underway to develop the required technology. Experts say that the residual monomer could be dropped by dilution with compounding agents and by the mixing action during such compounding.

Goodrich, for one, is already exploring possible approaches to removing the residual monomer, and plans to set up a pilot operation soon.—JMN

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New Catalyst Lowers Polypropylene Costs

Belgium's Solvay has a new catalyst that it claims can cut up to 20% off the capital cost of a polypropylene polymerization plant.

For 20 years, the U.S.'s Hercules and Italy's Montecatini have been battling over patent rights on catalysts used to make polypropylene. But that contest may now be academic: Hercules has just purchased a license from Solvay, and other big polypropylene producers are likely to follow suit.

What Solvay has apparently done is develop a catalyst that is 4-5 times more active than previous choices and yields a product with only 15-20 ppm of titanium catalyst residue. Thus, the expensive alcohol washing and purification steps that have been required to lower the titanium content below 100 ppm are not required.

The Old Way—The standard polypropylene catalyst now on the market uses trichlorinated titanium in the form of hexagonal or cubic crystals. These form tiny nodules or balls that are ball milled to obtain a larger surface for exposure to the monomer. The problem is that relatively large quantities of the catalyst often find their way into the polymer, harming the polymer's thermal and other physical characteristics. Also, the ball-milling process damages the surface of the catalyst crystals, which in turn affects the shape of the polymer particles.

Researchers have tried to overcome the titanium problem by increasing the catalyst surface area, thus cutting down the amount of catalyst required and thus the amount of carryover. One approach has been the use of porous nodules, but the problem has been that the percent of useless (atactic) polymer has risen from about 6% to 10%, thus negating the benefit of the increased activity.

Solvay's Way—The porous nodule approach was also chosen by Solvay, but with its version the atactic waste is only 4-5%.

Solvay's catalyst takes the form of tiny dense spheres that are 20-40 microns dia.; monomer seeps inside, breaking them into smaller fragments that finally measure only about 60 Å and are composed of 3-4 crystals each. The surface area thus achieved is up to 200 m^2/g, vs. only about 4-5 m^2/g conventionally.

To make the new catalyst, says the company, a standard trichlorinated titanium product is reduced in an organo-aluminum solution, then a complexing agent is added followed by a dose of quadrichlorated titanium—the very product that usually leads to atactic polymer.

Solvay is building an industrial-scale plant to produce the new catalyst, and is soon to start construction of a 50,000-ton/yr polypropylene plant due onstream by the end of 1975; expansion is planned up to an eventual 100,000 tons/yr. And Hercules has plans for a 100,000-ton/yr polypropylene plant in Belgium. #