VCM file

Getting out the last traces of VCM

Tenneco process uses activated carbon to remove vinyl chloride monomer from PVC plant gas streams. It's one of several methods producers are licensing

More than a year's experience with its carbon adsorption method of controlling vinyl chloride emissions from polyvinyl chloride plants has convinced Tenneco Chemicals (Saddle Brook, N.J.) that it has found the best route. So it is setting out to license the method to others.

When the cancer-causing properties of vinyl chloride monomer became known, explains Robert S. Miller, manager of polymers research, the firm had to develop its own technology to control emissions. Now it is marketing the know-how in the U.S. and in European countries that are following the U.S. lead in setting stringent emission standards.

The firm is just one of a number of U.S. producers that have developed licensing packages in an effort to recoup part of the millions they have spent to develop the new technology.

B.F. Goodrich is licensing its steam-stripping process, which removes VCM from PVC suspension resins. Diamond Shamrock has developed a proprietary technique for removing residual VCM from PVC dispersion resins. Monsanto has been licensing its PVC reactor cleaning know-how for more than a year. Lonza (Basle, Switzerland) is offering a procedure for preventing suspension resin polymer buildup on reactor walls. And several others have developed instrumentation to monitor the amount of VCM in the air and in PVC.

Thirsty Carbon: Tenneco's development is aimed at recovering the residual VCM in vent gas streams (*CW, Sept. 18, 1974, p. 66*). A unit built by Chemical Design (Lockport, N.Y.) was installed at Tenneco's PVC plant in Pasadena, Tex., in early 1975.

A year's experience with the equipment, says Roy T. Gottesman, associate director of research and development, shows that less than 4 ppm. of vinyl chloride monomer is escaping in the adsorber effluent stream. During that time, the activated carbon in the unit has undergone more than 1,300 adsorption and regeneration cycles. That makes it good enough to meet the proposed Environmental Protection Agency standard of 10 ppm.

Moreover, after 10 months of continuous service, samples of carbon withdrawn from the adsorber showed that it retained 90% of its original adsorptive capacity. Further, there was no evidence of vinyl chloride polymerization in the adsorption unit or within the carbon.

Trouble Spots: Aside from leaks, which manufacturers try to keep to a minimum, there are several points where VCM can escape to the atmosphere: at the reactor, the slurry tanks, and equipment purge streams.

PVC is made primarily by either suspension or emulsion polymerization techniques. Generally, in these processes VCM and the polymerization initiator are dispersed in water by the use of suspending or emulsifying agents. The polymerization temperature is selected to obtain the desired molecular weight. But not all of the vinyl chloride is converted into PVC. Usually 17-20% of monomer that does not react remains at the end of the polymerization cycle. Much of that can be recovered and recycled to the front end of the process. But as much as

TENNECO'S GOTTESMAN: New process cuts PVC plants' VCM loss to below 4 ppm.

4% VCM can remain in the PVC slurry from the reactor. That can be removed by specialized stripping techniques, such as the ones Goodrich, Diamond Shamrock and Tenneco now offer.

Residual VCM from that cleanup phase is one of the potential sources of feed for the carbon adsorption step.

Another source is the slurry tanks, where operators flush air or nitrogen through the vapor space of the tank to keep VCM concentrations down and prevent a flammable mixture from forming. Depending on the level of stripping of the slurry downstream, VCM concentrations in the nitrogen purged may reach 15 mol percent.

Various equipment in the process is also purged with inert gas to reduce the explosion hazard and to remove the last traces of VCM. These off-gas purge streams generally contain 10-30 mol percent vinyl chloride.

New Twist: Vinyl chloride has been around a long time and so has activated carbon. But up to now, researchers have worked with pure monomer. Tenneco's contribution has been to make the process work with recovered vinyl chloride, says Gottesman. He explains that this material can contain residual initiators, catalyst fragments, and suspending agents, so that it is prone to polymerize and foul the carbon system.

Making the process work is a matter of selecting the right operating conditions and the right type of activated carbon.

Another method of scrubbing VCM from stack gas, called oxyphotolysis, has been investigated by Robintech of Fort Worth, Tex. (*CW Technology Newsletter, July 9, 1975*). The firm says it is still evaluating the economics of installing the unit, which so far has not been used commercially.

Although carbon adsorption is the process that Gottesman believes will attract the widest interest, the company is arming itself with a variety of other technology. "We have filed 13 patent applications on widely differing subjects," says Gottesman. "They include a spray apparatus for cleaning PVC reactors, processes for removing VCM from suspension and emulsion processes, the destruction of VCM by ozonolysis and the removal of monomer from dispersion latex by sparging."

If others' experience is any indication, there is a big demand for the know-how. B.F. Goodrich Chemical says it has signed agreements with six corporations in Sweden, Italy, Japan and the U.S. for its suspension-resin stripping technology.

Diamond Shamrock became a licensor in March, offering its proprietary technique for removing residual VCM from dispersion resins. Different techniques are required for the two systems because of differences in particle size.

The company explains that in the suspension process, monomer droplets suspended in water typically produce PVC particles ranging in size from 90 to 130 microns. In the dispersion or emulsion process, a colloidal dispersion of monomer droplets creates PVC particles averaging 0.5 micron in size. These smaller particles are more sensitive to heat and mechanical disturbance than suspension resins, thus different technology is required.

Says Diamond Shamrock, "We are using it ourselves. We have a number of people seriously interested, including some from outside the U.S. We do not at the moment have any licensees. But it is a relatively new offer."

It seems doubtful that anyone will reap a financial bonanza from the new technology. Rather, licensors see their effort as one of trying to recover part of their development cost.

Diamond Shamrock adds: "Licensing this kind of technology is not going to be a giant money-maker for anybody, as far as we can see, once you put the income generated up against what it cost to develop it in the first place. We hope we will be able to defray our developmental costs—that is, spread them out through the industry."

Insight into energy

A new 900-page United Nations study of energy use has turned up extensive data on the use and distribution of commercial energy since 1950. Among the findings:

- The U.S., with 5% of the world's population, used 30% of the world's commercial energy in 1974, compared with 45% in 1950. Its per-capita gasoline consumption was nine times the world average.
- The U.S.S.R., the world's second-largest user, increased its share from 11.5% in 1950 to 16.6% in 1974.
- China and Japan are the third- and fourth-largest consumers, respectively. China still relies mainly on solid fuel. Japan is a leading importer of all types of energy.

The report updates earlier studies on commercial energy production, trade and consumption and includes preliminary data on the production of primary fossil fuels for 1975.

It is available from the UN Sales Section (New York) for $30.

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