

Unloading and storage technique for vinyl chloride monomer

The system described here is critical to the safe handling of this widely discussed carcinogen.

Asu Mukherji, Catalytic Inc.

Numerous tests and consequent governmental regulations have established vinyl chloride monomer (VCM) as a dangerous carcinogen.* Manufacturers of VCM have accordingly modified plants to protect workers from contact with the chemical.

In the changeover, one step has become critical to the overall process for converting toxic VCM to safe polyvinyl chloride (PVC)—the loading step, where VCM from tank cars and tank trucks is loaded into a customer's storage tanks for processing to PVC. Since the polymerization plants are relatively smaller than VCM plants, and are dispersed near to their markets, the critical loading stations are many.

Moreover, vapors from an empty VCM storage tank must be collected and contained as they are displaced by a new supply of liquid, because of stringent specifications as to permissible concentrations of VCM in the atmosphere.

Still further, VCM is an explosion hazard, corresponding to Class I, Group D, Div. 1, of the National Electrical Manufacturers Assn. code, NFMA 7, and variations in ambient temperatures at various locations complicate the outdoor unloading/loading problem.

Vapor/liquid exchange

The key to solving these problems consists of a vapor-liquid-exchange process, which has been incorporated into the design of a number of successfully operating unloading stations (Fig. 1). With this process, the compressor draws vapor from the plant's storage tank, and feeds the compressed vapor into a tank car, forcing VCM from the tank car up through a dip tube and into the transfer piping system.

Alternately, a slipstream of liquid VCM from the storage tank is vaporized by steam to similarly increase tank-car pressure. The vaporizer generally comes into play either when the compressor is down for maintenance or when ambient temperatures are too low (below 60°F) for the compressor alone to handle the unloading.

Using the compressor, VCM transfer continues until the level in the tank car falls below the dip pipe, at which point the tank car is full of displaced vapors plus

residue liquid. This liquid can be transferred by connecting the compressor's suction to the tank car, and its discharge to the storage tank. A four-way valve in the suction and discharge lines effects this changeover without exposing the operator to VCM.

With the normal compressor flow thus reversed, residual liquid in the tank car vaporizes from the reduction in pressure, while the compressed vapors are condensed in the storage tank by bubbling them through the large mass of liquid, which removes the heat of compression. In this manner, the tank car is normally evacuated down to the pressure required for reloading.

Depending on the heat transfer into the tank car, residual liquid vaporizes within 20 to 30 minutes, during which time the pressure will not be radically reduced. After the liquid has been vaporized, the time for evacuating the remaining vapors may be calculated with the formula:

$$M = (V/DE) \ln (P_1/P_2)$$

where: M = evaporation time, min.

V = tank-car volume, ft.³

D = compressor piston displacement, ft.³/min.

P_1 = tank-car pressure at start of cycle, psia

P_2 = tank-car pressure at end of cycle, psia

E = average volumetric efficiency of compressor

The economics of the evacuation operation can be evaluated according to the value of VCM.

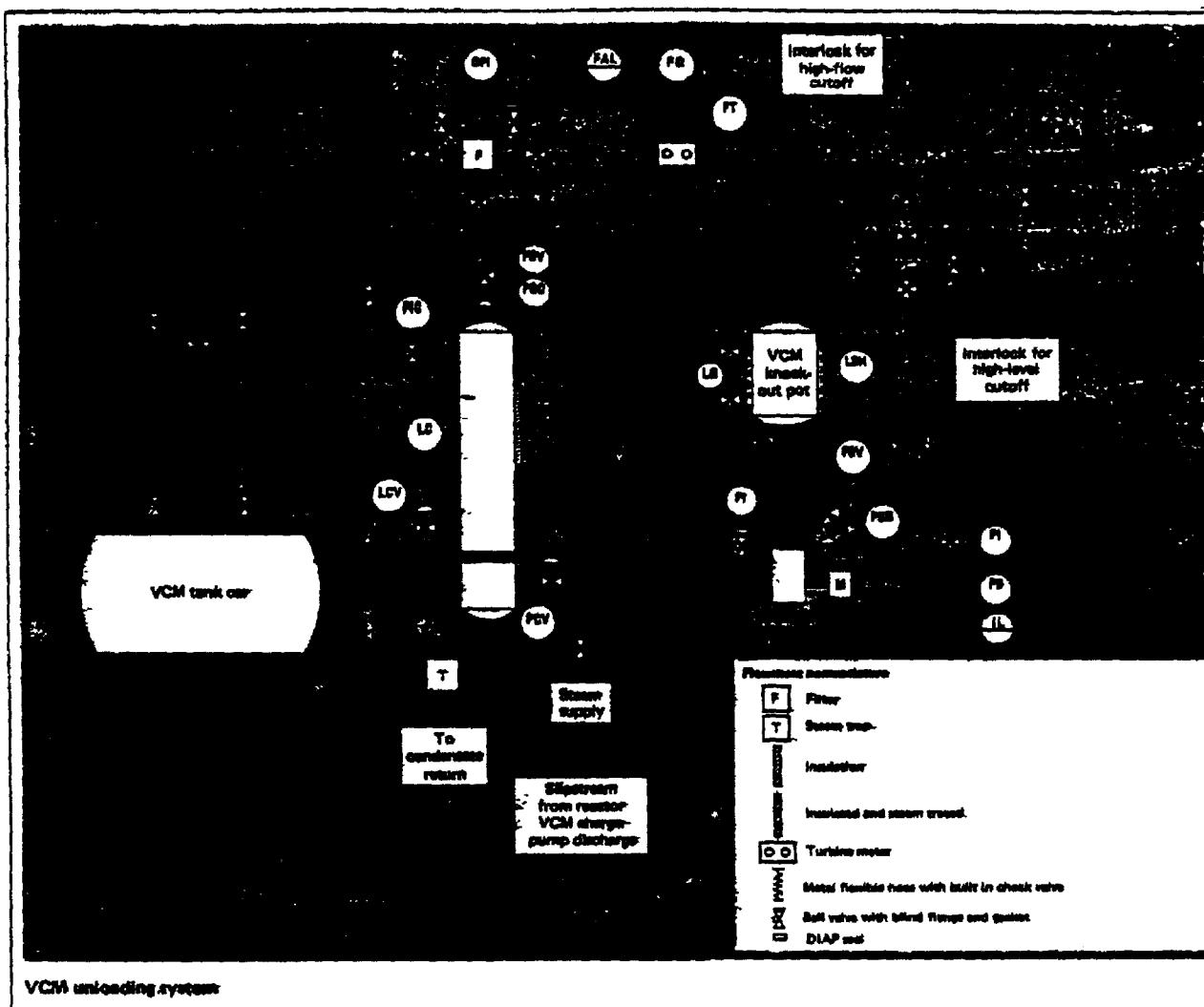
After the tank car has been completely evacuated, the compressor is used to evacuate the disconnected hose, which only then should be taken off for storage.

The storage tank is emptied of VCM for maintenance by filling it with water as displaced vapors are vented to a monomer gas collecting system, and then letting in air through the atmospheric vent as the water is drained into the diked storage area for runoff to storm sewers.

Unloading system

The unloading system consists of transfer piping, compressor, vaporizer, storage tanks, and instrumentation for safety and control. Flexible metal hoses connect the tank car to the rigid transfer piping. Each transfer connection on the tank car contains an isolation valve and a built-in excess-flow valve to prevent leakage in

*Chem. Eng., May 13, 1974, p. 35; July 8, 1974, p. 28; Sept. 2, 1974, p. 23; Sept. 30, 1974, p. 23; Sept. 30, 1974, p. 42; Feb. 17, 1975, p. 35; Mar. 17, 1975, p. 23; June 9, 1975, p. 36; Oct. 15, 1975, p. 67; Jan. 5, 1976, p. 74



the event of a ruptured hose. Similarly, the rigid piping contains check valves to prevent backflow from the storage tank in case of rupture.

VCM inventory is measured by means of a turbine meter and a flow totalizer in the transfer piping. A filter upstream of the meter protects it from dirt, as well as extending the online time of the monomer-reactor charging filter (see Fig. 1).

Design criteria

The steps in designing a vcm-unloading system generally take the following sequence:

1. Establish the piping configuration for compressor, vaporizer, storage tank and tank car.
2. Determine the optimum transfer-line size for the desired flowrate.
3. Size and select the compressor.
4. Develop the detailed instrumentation.

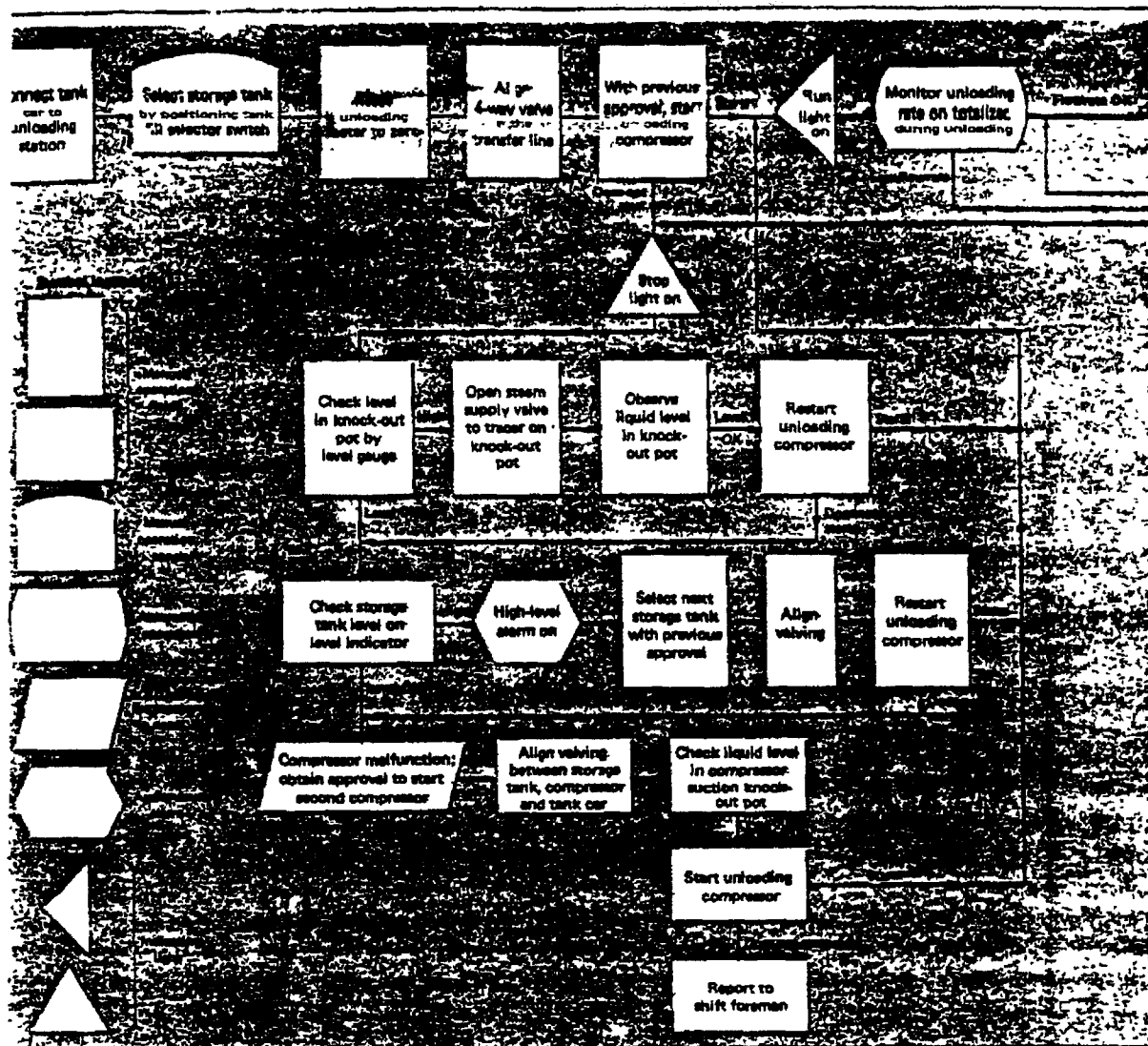
The piping configuration is made in accordance with

the flow scheme (Fig. 1) and a physical layout for the unloading station. Pressure drops in the transfer lines must include static elevation and line losses between the compressor discharge and the tank car, and between the compressor suction and the storage tank. Also, pressure drops across the turbine meter, and a dirty filter, must be allowed for.

Since the entire unloading area will be outdoors and may be in northern climates, the compressor and vaporizer design must allow for seasonal temperatures such as 110, 60, and 10°F, corresponding to monomer vapor pressures of 95, 43 and 11 psia, respectively.

A common practice is to size the compressor for spring conditions, relying on the vaporizer to augment transfer during the winter. In this case, the compressor will unload during summer at a much faster rate, which can be calculated by trial and error, assuming a flowrate and working backward through the compressor-sizing calculations.

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Operating diagram for unloading vinyl chloride tank car

Fig. 2

and accumulates the actual vcm removed on both a stable batch counter and a continuous counter, in order to be able to display vcm unloaded from several cars after a period of time. The batch counter is dogged after unloading each tank car, and before unloading the next.

To compute a material balance, a reactor batch weight, and a reaction conversion, the operator must know the total weight of vcm unloaded into the storage tanks. Since the density of unloaded vcm varies with ambient temperature, a temperature-compensated flow measurement is required.

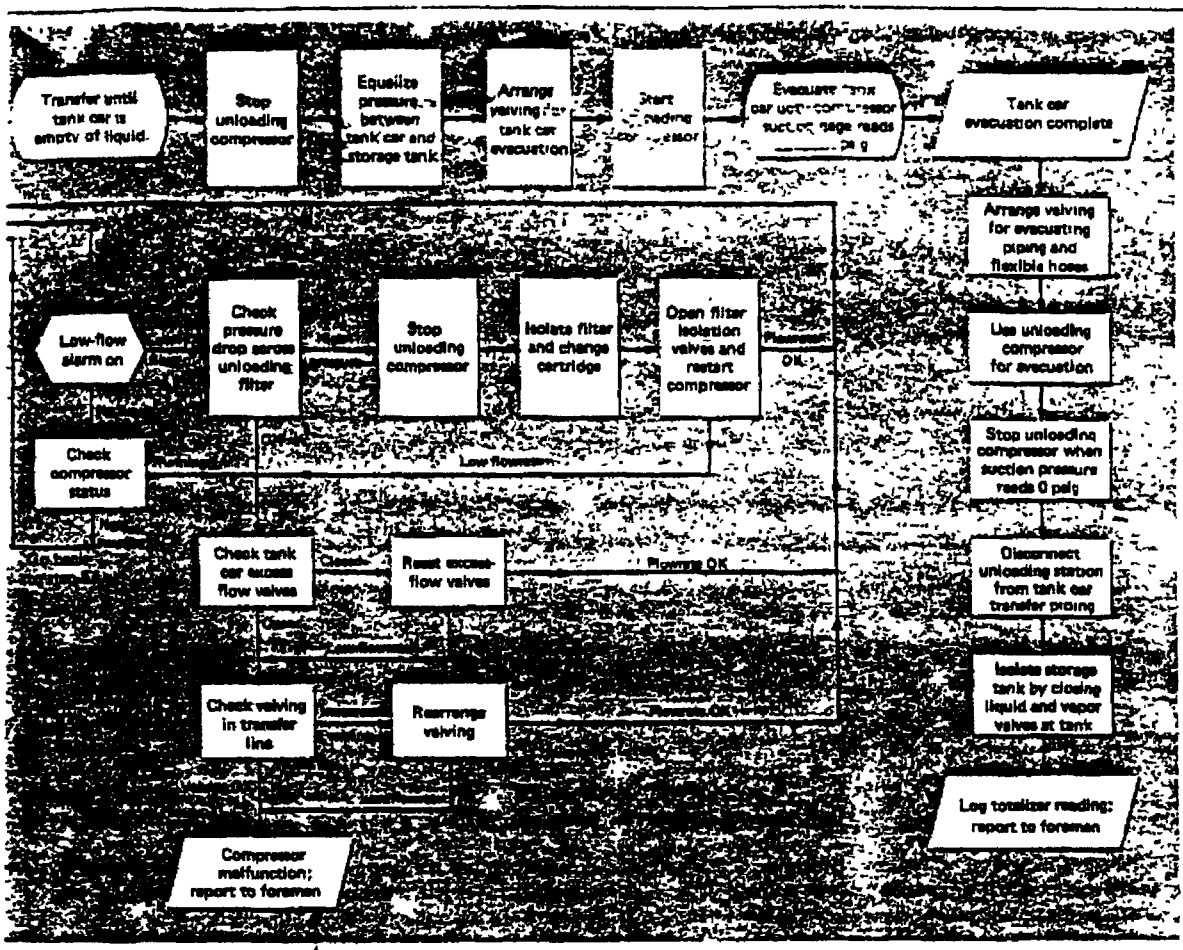
The turbine meter affords an accuracy of ± 0.15 to 25% of the instantaneous flow. For such accuracy, meter vendors must have density and viscosity data

for seasonal conditions. Also, the transfer line must provide straight runs of 15 pipe diameters upstream and 5 pipe diameters downstream of the meter.

The totalizer should have built-in low-flow and high-flow switches. The low-flow gives indication when (1) the filter ahead of the meter is plugged, or (2) the manual valves in the transfer line are blocked, or (3) the compressor is malfunctioning. The high-flow protects the turbine meter from overspeeding due to vapor flow, by stopping the compressor. Vapor flow occurs when the liquid level in the unloading tank car drops below the dip pipe. Overspeeding the turbine reduces the life of its bearings and may damage the rotor. Even after the compressor stops, vapor flow will continue until the tank car and storage tank have achieved the same

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pressure, which can introduce significant error in the totalized reading.

This vapor flow can be avoided by placing an automatic on-off valve, actuated by a density-difference or pressure switch, at the tank-car end of the transfer line.

The level indication on a storage tank permits scheduling that tank for reloading and production, whether the tank has enough material to charge a reactor batch or whether a tank car's contents can be unloaded into it. Magnetic and capacitance-type level meters provide a reading unaffected by the varying VCM density. Readings that depend on liquid pressure, on the other hand, will vary with ambient temperature.

A high-level switch interlocked with the storage-tank unloading pumps prevents cavitation by maintaining enough liquid head at the pump suction.

In the event of fire, an automatic fire-valve on the storage tank's discharge line isolates the tank. Normally, a fire-safe full-port ball valve with pneumatic actuator serves for this purpose. The fire detector can be a bimetallic switch set at 170°F near the fire valve. A relief-valve/rupture-disc combination protects the storage tank from overpressure due to fire or overfilling. A

redundant relief system on each tank prevents accidental shutdown.

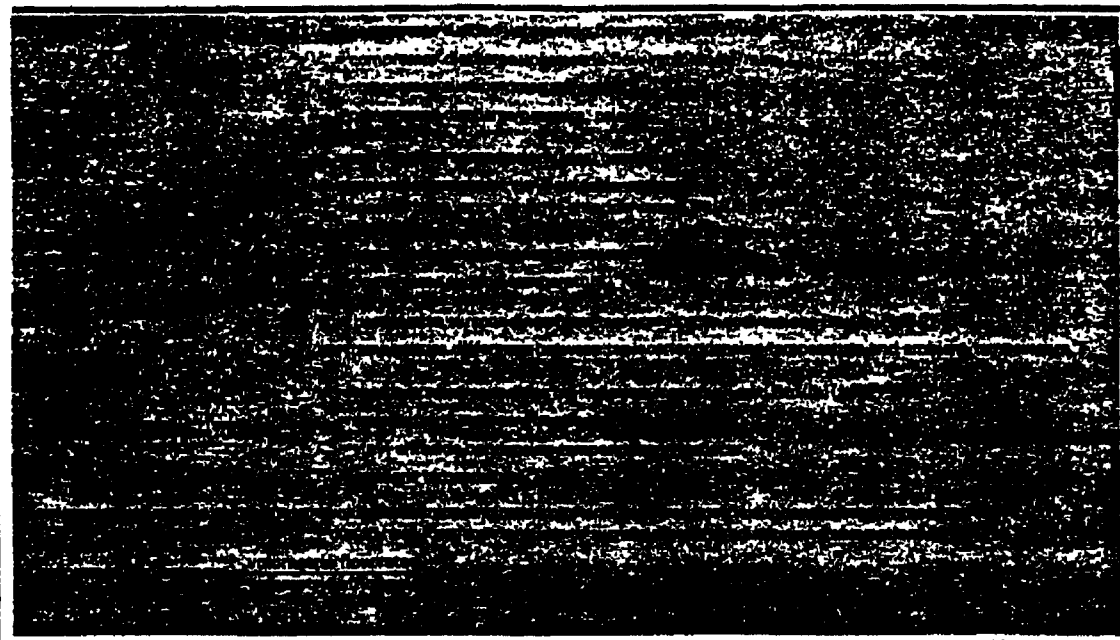
A self-actuated excess-flow valve downstream of the fire valve isolates the storage tank in case of line rupture, or failure of the reactor charge-valve, or an instrument malfunction in the VCM-reactor charging system. Fire and excess-flow valves are close-coupled to the storage tank and interlocked with the storage-tank unloading pump to prevent evacuation of pump suction lines with these valves closed, and thereby prevent overheating the pump.

For multiple storage-tanks using several unloading compressors and unloading pumps, the installation requires multiposition selector-switches to facilitate automatic interlocking of the selected tank instruments with the pump and compressor in use. Instrumentation for the compressor includes gages to display discharge pressure, and a relief-valve/rupture-disc combination to protect positive-displacement compressors. It is not good practice to pipe the discharge of this valve to the compressor suction, because of possible overheating due to continuous recirculation and recompression.

A liquid trap on the compressor suction side

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Expressions used to calculate compressor displacement



mizes chances for slugs of liquid to reach the compressor. A high-level switch in the liquid trap is interlocked to shut down the compressor, and the trap is steam-traced and insulated to reduce the accumulation of liquid. Instruments for the compressor and liquid traps generally come as part of the compressor package. Pressure and level controls on the vaporizer aid the unloading operation by maintaining heat and material balances, respectively. Pressure is maintained through the heat input to the vaporizer, and the level is held constant by liquid VCM flow.

Since the vaporizer operating pressure is higher than the storage-tank pressure, the storage-tank unloading pumps must supply a slip-stream of chloride to the vaporizer. Possible cavitation damage to the level-control valve can be eliminated by means of a valve with a high recovery coefficient or anticavitation trim.

A relief-valve/rupture-disk combination protects the vaporizer from overpressure due to fire, or steam-valve or level-valve failure. The steam valve is interlocked with the high-flow cutoff switch of the unloading system protecting the turbine meter.

Safety

Area monitors are located at breathing level in the work areas to detect VCM emissions. Since vinyl chloride vapor is heavier than air, it has a tendency to move downward, so detectors for combustible gases should be located at an elevation of $2\frac{1}{2}$ ft, near the sources of possible VCM vapor leaks.

VCM concentration, measured in ppm by a chromatograph, is displayed, and an alarm sounds when this concentration exceeds 75% of maximum permissible.

VCM concentration as a percentage of VCM's lower explosive limit is also displayed, monitored and alarmed—as measured by a remote combustibles analyzer. Because of the distance between the polymerization-reactor control room and the unloading area, it is usually convenient to group controls and instruments for VCM unloading on a nearby water- and dust-tight control panel. The control room operator needs only the critical data for overall coordination—such as storage tank level; and the status of the unloading compressor, the fire and excess-flow valves, and the unloading pump. A remote pushbutton can be interlocked with all the fire valves on storage tanks, in order to close those valves in an emergency.

Relief valves protect the transfer piping from thermal expansion wherever liquid can be blocked between valves. The blinded vent on the storage tank is equipped with a flame arrester to prevent flash-back into the tank.

The author



Asa Mukerji is a senior instrument engineer with Catalytic, Inc., 1500 Market Street, Philadelphia, Pa. 19102, where he has served as lead instrument engineer for a variety of projects. He has had prior design and application experience with an instrument manufacturer in India. He holds an M.S. degree from Drexel University and a B.S. degree from the Indian Institute of Technology, Bombay, in chemical engineering.

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...has been increasing rapidly for several reasons. One is merely the greater interest in natural resistance as an alternative to chemical pesticides. Also, natural product chemists are becoming more aware of the opportunities for research in the field and new microchemical techniques are making such research more feasible. Perhaps most important is the fact that the Food & Drug Administration is expected to issue regulations to ensure that changes made in plants to develop resistance also won't constitute hazards to the health or nutrition of humans and other animals that eat them. Chemical research will be required to obtain the evidence and documentation necessary to comply with the regulations.

Better understanding of the mechanisms of resistance at the chemical and molecular level also will simplify the plant breeder's work, according to Dr. Anthony C. Waiss, a phytochemist at USDA's Western Regional Research Center, Albany, Calif. "The present lack of this knowledge," he says, "has forced plant geneticists to rely on 'correlative factors' such as color of flower or shape of leaf, but guided their breeding programs. That's a somewhat like assuming that a person's intelligence can be judged by his nose, adding that the use of unselected traits as correlative factors often has misled plant breeders."

Consequently, Waiss and his group are working to improve the efficiency of plant breeding by isolating and identifying the chemical substances responsible for resistance, and by finding out how they operate in nature. For example, chemists at the USDA laboratory have recently identified two different toxins from sunflower that are toxic to sunflower moth larvae. They also have found that tannin in cotton may play a major role in imparting resistance to the cotton budworm, and that certain polyphenols protect corn against earworms.

Results so far suggest that compounds imparting natural resistance are more selective in their toxicity and are strategically located in the plant to affect target insects. "Because of the effectiveness of this delivery system," Waiss says, "these resistance factors we've found so far show very low toxicity compared to chemical insecticides." Waiss emphasizes, however, that "resistance" and "susceptibility" are relative terms, not absolutes. And, he points out, age and habits of the plant, environmental factors, and insect feeding behavior also play important roles in the total scheme.

At USDA's National Cotton Pathology Laboratory, College Station, Tex., Dr. Robert D. Stipanovic, working with Drs. Alois A. Bell and Texas A&M chemist Daniel H. O'Brien, has found that cotton leaves and flower buds contain several natural "helicoides"—terpenoid aldehydes that are toxic to heliothis species, including the cotton bollworm and the tobacco budworm. At least 10 related compounds are involved. Stipanovic notes that only a single leaf is needed to reveal which helicoides are present, and in what

amounts in a cotton plant. A three-man team analyzing leaf extracts by thin-layer chromatography can screen 240 "progeny" per day—which is easier and quicker than waiting to see which plants the worms eat and which ones they don't. "Our understanding of the structures and biosynthesis of the cotton terpenoids is allowing us to predict what can and cannot be accomplished to increase host plant resistance by genetic manipulation," Stipanovic comments.

Of course, plants must resist diseases as well as insects. According to Dr. Noel T. Keen and Dr. Berndt Bruegger, plant pathologists at the University of California, Riverside, at least 75 species of higher plants are now known to make "phytoalexins," or chemical compounds that help ward off infection. These are low-molecular-weight substances, such as terpenoids, isoflavonoids, and phenols, that a plant normally produces only after it has been infected by pathogens. Whether and to what extent a plant produces these antibiotic compounds determines its resistance or susceptibility to disease. It's not really desirable, Keen says, to try to breed plants that produce large quantities of phytoalexins; they tend to be quite toxic. Rather, the goal is to find the chemical factors—"elicitors"—that pathogens then stimulate phytoalexin production.

Whether these elicitors are specific or general in their action is the subject of some controversy. However, Dr. Barbara S. Valent and Don Peter, Albersheim, chemists at the University of Colorado, Boulder, believe that they are non-specific. That is, diverse plants will respond to stimulation by a single elicitor. They propose, for example, on the basis of their work with soybeans, that structural glucans found in the cell walls of many fungi play a general role in plant resistance to infection by fungi. They note that a glucan-containing fraction "extracted" from brewer's yeast (normally a nonpathogen) is just as effective in stimulating soybeans to synthesize phytoalexin as is the glucan from pathogenic fungal varieties. Valent and Albersheim also suggest that application of elicitors could, by activating plant defense systems, reduce the need for conventional chemical pesticides.

Phytoalexins alone can't entirely account for disease resistance in plants, say Dr. Joseph Kuc and Dr. Frank E. Caruso, of the department of plant pathology at the University of Kentucky, Lexington. They note that much "protected" tissue in plants contains no phytoalexins. Rather, it appears that at least three mechanisms must be coordinated to provide the protective response to infection. One restricts penetration of pathogens into the plant. Another causes the pathogens to clump, inhibiting their spread through tissues. A third mechanism hinders the growth or multiplication of the pathogens. Also, Kuc notes, agglutins in the plant may react with enzymes and toxins produced by the pathogens, thus abating the symptoms of the disease.

An important finding is that plants can be protected from disease in ways that resemble those used to immunize animals. Experiments with watermelons, muskmelons, and cucumbers showed, for example, that inoculation of just one leaf of a young plant with a pathogenic fungus would produce lesions on that leaf and the leaf would die. However, Kuc says, the limited infection stimulated a protective response that spread through the growing plant. The effect lasted four to five weeks. A "booster" inoculation, three weeks after the first, extended the systematic protection through the fruiting period.

Experiments to find the "chemical signal" that turns on the immune system are now under way, Kuc notes. If found, he says, it could eliminate the need to use living organisms to impart protection; seeds could be treated with the chemical, thereby immunizing the germinating seedlings.

Class of rearrangements dubbed bicycle reactions



Bicycle enthusiasts may be happy to learn that they have allies in the molecular realm. Dr. Howard E. Zimmerman of the University of Wisconsin, Madison, told the symposium on organic photochemistry, sponsored by the Division of Organic Chemistry, of a class of light-induced reactions he calls "bicycle reactions." As he describes one such reaction: "The C-6 of a 2-methylenebicyclo[3.1.0]hex-3-ene sits along the pi system of a fulvene moiety to the exocyclic pi bond, thus giving a spiro[2.4]hepta-4,5 diene. The rearrangement can be envisaged as involving a carbonoid carbon (for example, C-6) bicycling on the fulvene pi system using its sp² hybrid orbitals as 'wheels' and its exo and endo substituents as 'handlebars.'" Although it is not clear where the pedals are attached, they seem to turn in only one direction; Zimmerman and his colleague Timothy P. Cutler have shown that except in special circumstances, the carbonoid bicycle will move only counterclockwise around the ring. They describe three more examples of the reaction in a paper submitted to the *Journal of the American Chemical Society*.