VINYL CHLORIDE MONOMER STRIPPING OF PVC RESINS

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As mentioned in our earlier discussions on reactor cleaning, the two major sources of vinyl chloride emissions in our PVC manufacturing plants were from reactor opening and residual vinyl chloride in the PVC resins. Although both were important, the foremost problem we faced commercially was to reduce the residual vinyl chloride monomer (RVCM) in our PVC resins. The high levels of RVCM (10-30,000 ppm) at various points in process was a major source of worker exposure and emission to the atmosphere. In addition, the RVCM in the final dried resin was sometimes high enough to expose our customers during subsequent melt processing.

When we embarked on our program it was immediately apparent that we needed to supplement our basic information on vinyl chloride solubility and diffusion in PVC. This was necessary not only to define how best to eliminate the vinyl chloride monomer (VCM) but also to define the levels at which RVCM would no longer be a hazard to handle by both our customers and our own workers. The basic data was obtained by A. R. Berens of our Corporate Research group and is well documented in the literature (1-8). Simultaneously, exploratory studies on paper and in the laboratory were initiated on various approaches to reduce or eliminate RVCM. These approaches included postpolymerization to remove the vinyl chloride in-situ. This was quickly abandoned when our kinetic data indicated very high levels of initiator would be required, thus increasing costs significantly not to mention the negative impact on resin properties.

Beren's early work immediately showed that VCM followed normal Fickian diffusion and was, therefore, strongly influenced by temperature and particle size or in the case of suspension PVC - particle structure. His work oriented our program in two directions: engineering - mechanically stripping the RVCM out at higher temperatures and, polymer chemistry - modifying the basic PVC polymer structure to permit more rapid RVCM removal. Although both approaches were aggressively pursued we rapidly zeroed in on stripping, either batch or continuous, as likely the best and most rapid solution to the problem. While batch stripping was pursued on a pilot scale and in our production plants, a small pilot plant stripping column was installed at our Brecksville R&D Center. Although batch stripping at higher temperatures significantly reduced the RVCM levels, the pilot stripping column work quickly indicated this would likely be the most efficient route.

As a result of this work, a prototype unit using a modified distillation column was constructed and installed at our Avon Lake, Ohio production plant. Engineering data, resin quality data, and RVCM levels at various stripping conditions were obtained from this unit for design of the commercial units. This unit is still in operation today in one of our polymerization lines at Avon Lake, Ohio. Again, data verified the favorable results of the pilot plant stripping column and permitted optimization of operating conditions and procedures.

The commercial stripping columns were designed so they could be skid-mounted and shipped to each of our plants for immediate installation. This technique allowed each plant to do their own pre-engineering and construction so that when the unit arrived only utilities and process tie-ins were required. Stripping units were built for all five of our plants and installed as they were completed. The development from initial laboratory stripping to completion of final design took approximately 10 months. Installation of the commercial units were completed 12 months later. Although the development and design appear to be straight-forward, it was unique at the time in that stripping PVC above its Tg was generally felt to be highly harmful to PVC thermal stability and particle structure.

The stripping column is relatively straight-forward as shown in Figure 1. When the polymerization reaction is complete the batch is transferred to a pressurized stripping column feed tank. This tank functions to release excess VCM pressure back to the recovery system and to form the transition from the batch polymerization reactors to a continuous operating stripping column. PVC slurry is pumped from the feed tank to the stripping column through a small vapor-liquid separator. The vapor stream is directed to the top of the stripping column where it exits with the stripped VCM. The slurry enters the stripping column and flows downward counter-current to the steam injected into the bottom of the column. Counter-current contact between the two streams strips the residual VCM from the slurry and forces it to exit from the top of the column. The vapor is passed through a condenser into the vapor-liquid separator. The vapor from the separator which is primarily VCM containing a small amount of water vapor is piped to the conventional VCM recovery system. The liquid from the separator, which is water with a small amount of soluble VCM, is pumped back to the stripping column for additional stripping. Stripped slurry is pumped from the bottom of the column to a blend tank or directly to the centrifuge, dryer and storage bins for packaging or bulk shipment to customers.

There are obvious methods for improving energy utilization in the design, and we have now incorporated some of these into our present operations. The conventional VCM recovery system as shown in Figure 2 is a series of compression-cooling steps to condense and recover the VCM. The vent from this system can be handled by incineration, solvent absorption-desorption, or activated carbon absorption. Goodrich has chosen the solvent absorption-desorption system.

BFGoodrich Continuous Slurry Stripping System

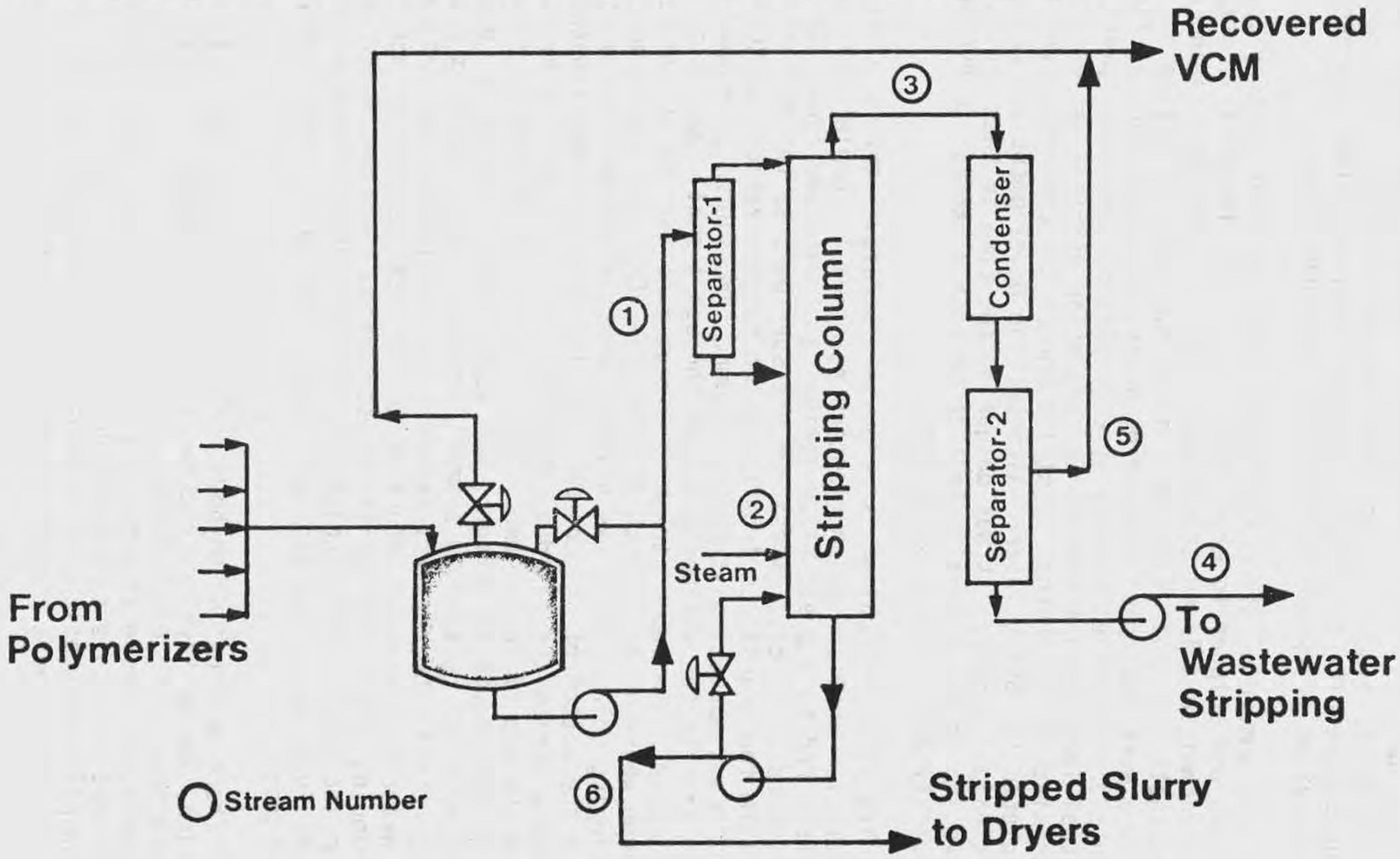
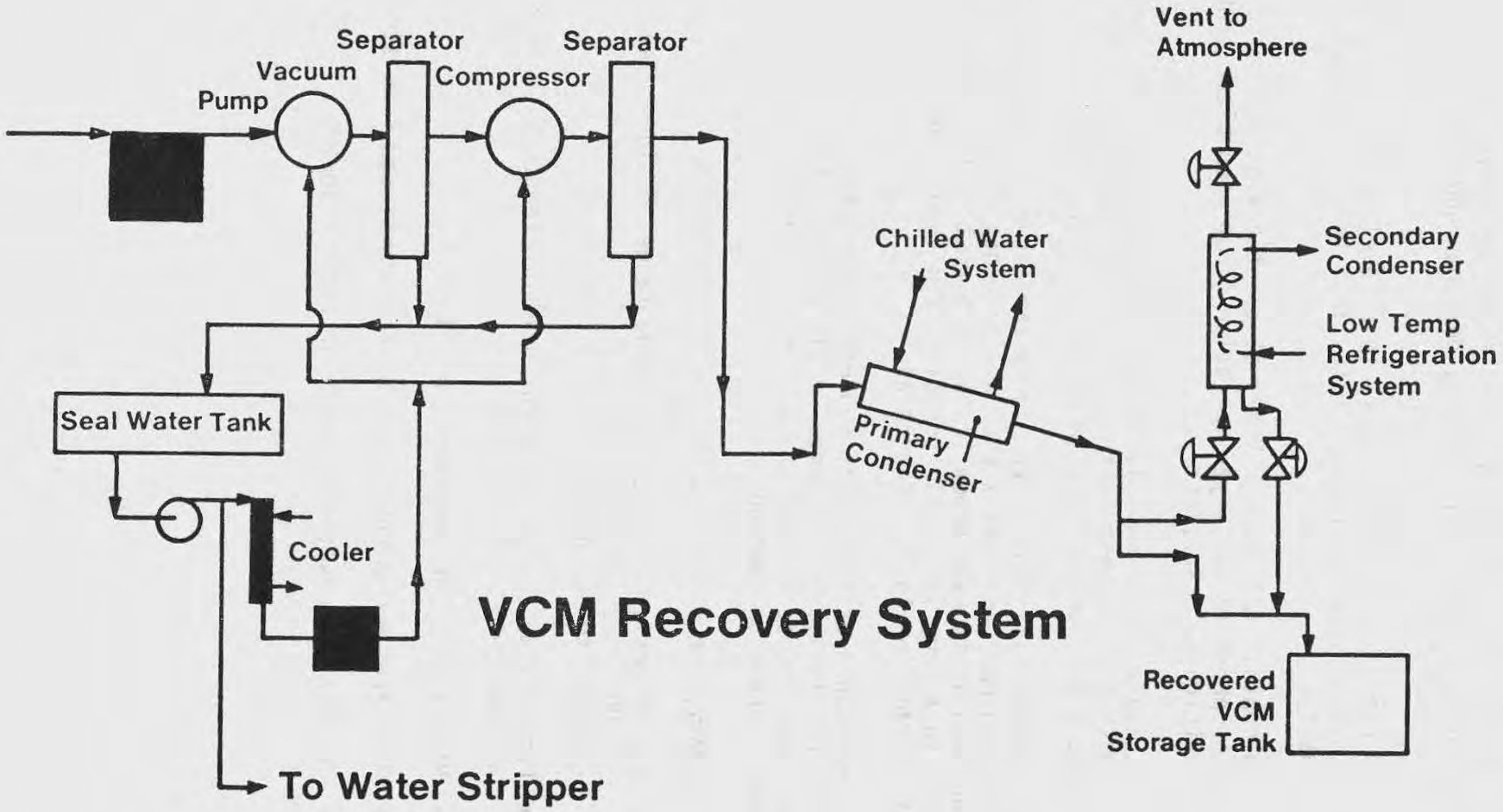


FIGURE 1.


Separator
Vacuum
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Separator
Compressor
Vent to
Atmosphere
Chilled Water
System
Secondary
Condenser
Low Temp
Refrigeration
System
Seal Water Tank
Primary
Condenser
Cooler
VCM Recovery System
Recovered
VCM
Storage Tank
To Water Stripper

FIGURE 2.

Figure 3 shows an installed Goodrich continuous counter-current stripping system. The two tall structures are stripping columns. As I noted earlier, these were a prepiped package design skid mounted for direct shipment and installation. Utilities and process streams could then be piped directly to the unit for rapid shakedown and startup. The slurry stripping process when properly designed and operated fulfills our three-fold objectives:

1. To reduce RVCM in PVC slurry to a level so that the dried finished product resin contains less than 1 ppm RVCM (dry resin basis).
2. To contain and recover VCM that is otherwise vented to atmosphere in the dryer operation (from open blend tanks, centfigure, dryer, etc.).
3. To operate continuously so as to afford better and more consistent process control (as to temperature, residence time, etc.) and hence result in better quality resin.

This process will handle PVC slurry streams with a wide range of RVCM (200,000-5,000 ppm) and resins with a wide range of particle structure. Our production units have demonstrated on a routine basis that RVCM can be removed to a very low level, normally less than 1 ppm, without any apparent degradation to PVC properties.

As I mentioned earlier, this process is operating commercially on suspension PVC in all of our domestic PVC plants. The process was made available for license in 1975 and is presently being used by a number of PVC producers here and abroad.

In summary, the continuous PVC stripping process:

- Can be designed to handle a wide range of slurry feed.
  - 5,000 - 200,000 ppm RVCM
  - Porous to non-porous particle structure
- Provides an energy efficient means to reduce RVCM to <10 ppm without harming PVC resins
- Minimizes worker exposure to VCM
- Minimizes emissions to atmosphere downstream from stripping
- Improves recovery efficiency of vinyl chloride

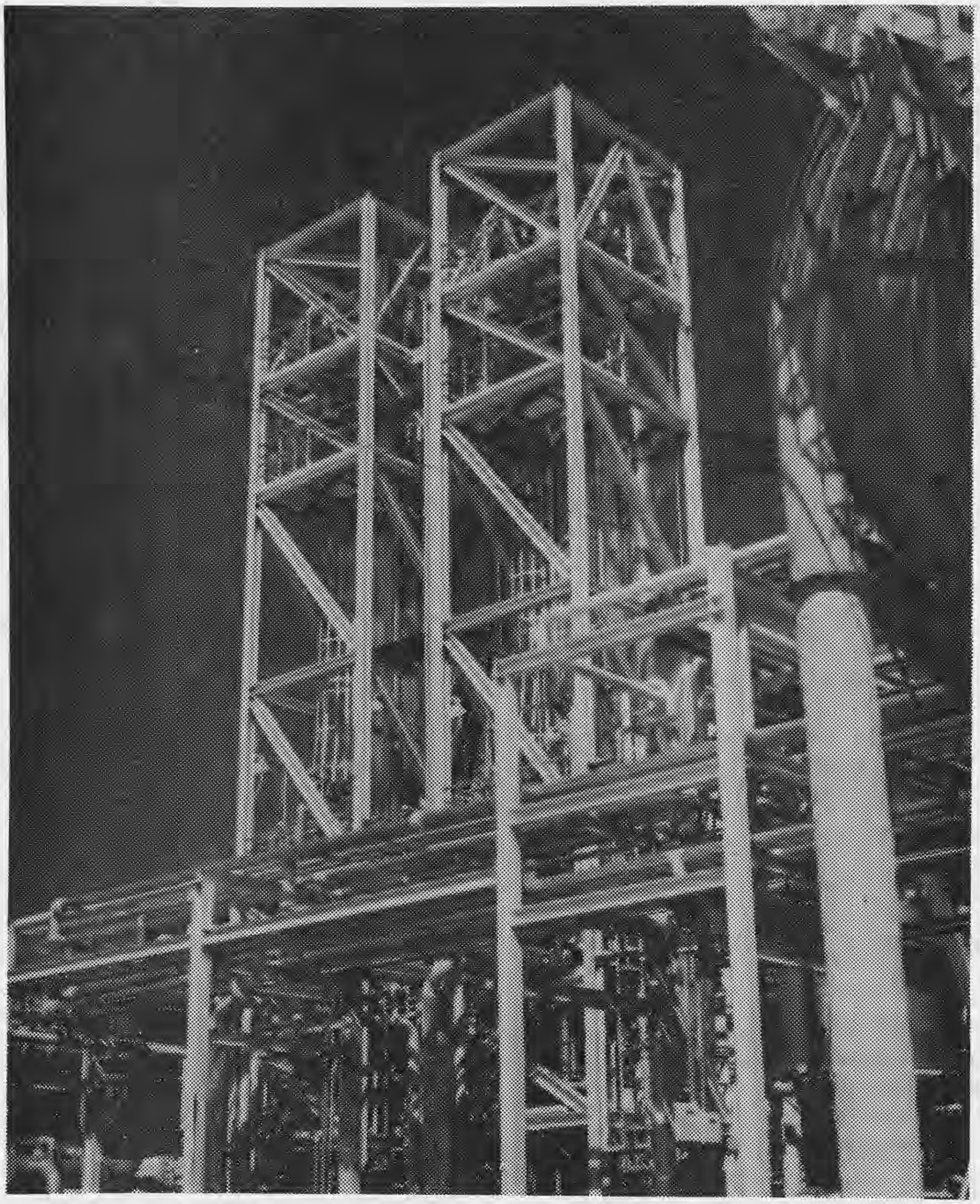

Figure 3. Installed B. F. Goodrich continuous counter-current stripping system.

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DISCUSSION:

MR. JOHN T. BARR: Is this correct that this can be obtained over all types of polymers or limited to certain molecular weights? Have you worked on copolymers on this?

MR. FRED KRAUSE: In general, the answer is yes for all molecular weights. We have done work with copolymers. We do not domestically manufacture a copolymer commercially. We have work based on the data there and we feel that we can design systems to handle copolymers. We have also worked with a very nonporous resins, blending resins, and those that we could use the technique to do that. The design of the system itself has to be looked at fairly carefully--because these types of resins are more difficult to strip.

MR. JAMES A. GIDEON: Could you comment on what your experience has been with licensing this technology. Has it proven to be profitable? What factors figure into the licensing of technology rather than keeping it to yourself?

MR. KRAUSE: I cannot directly answer the question of profitability, because you have to balance out what we have gotten out of licensing versus development. It should be a profitable venture for us because of the number of licenses. It was very early when the decision was made by Goodrich to offer this technology to the industry because of the severity of the problem. I think there may have been some question as to whether or not prior to the vinyl chloride problem, we would have necessarily gone out and licensed the technology. It was done specifically to address a problem.

MR. GIDEON: Do you have any thoughts on any way that the Government might serve to encourage more licensing of proprietary technology like that by technically advanced companies?

MR. KRAUSE: It is a difficult question to answer, because any company that's in a commercial business looks at their technology on a basis in terms of what it can return to them. A licensing decision is based on business in general, and you only license because it looks like it is going to be more profitable than if you kept it to yourself. It is a competitive business, and I guess other than incentives I don't have a good answer about how the Government can encourage that.

MR. BARR: Industry has been accused of being as bad as the special interest groups, running to the Government and saying, do things to protect us. But, here's one case where perhaps that could be justified, in that if it were considered to be enough of a social benefit that all society wanted to pay for this, then you could make the revenue from licensing proprietary information tax free; that would encourage the license process. That's sort of a socio-economic decision the Government has to make. That is one way to encourage it.

MR. RALPH C. BARLEY: I would like to offer an opinion. First, I understand that the stripping is directly connected with compliance. In other words, it stems from EPA findings which by now are part of the Federal Register and Federal law. Stripping represents compliance with those regulations. I think the industry would be very much encouraged to license technology which they have developed in this kind of connection, and to directly relate it to something that John said near the end of his talk, namely, that Government should not restrict industry too much so that it can't develop new technology. Am I on the right track?

MR. JOHN BARR: So far you sound good.

MR. GIDEON: In the course of NIOSH control technology studies such as the present one on plastics and resins, it has really been frustrating to see that much of the most innovative and effective technology for protecting workers cannot be widely used because of proprietary concerns. In my opinion, resolution of this area in order to permit technology sharing for purposes of providing improved worker protection is one of this most important issues which we all face.

MR. KRAUSE: I certainly agree with you, and I would like to reiterate that in the case of stripping, particularly, and to some degree from the reactor coating technology, the criticality of the problem and the exposure to employees dictated Goodrich's decision to offer licenses. Again, it is at some point, it had to be a business decision, because your whole industry is based on profit.

MR. ROGER HALL: My company is concerned with reducing levels of the monomer to the lowest level. I am asking the speakers and anyone else about acrylonitrile. We tried stripping it in the lab, and we're hunting for other methods.

MR. KRAUSE: I can't speak directly on acrylonitrile. Again, we found the diffusion of monomers in polymers is relatively close to the same. There are some monomers that have a high affinity for polymer itself, and as a result do not want to leave.

MR. TELESCA: Our next speaker will be Tod Delaney on leak prevention, proper selection and maintenance of equipment, seals, et cetera. Dr. Delaney obtained his degree in Environmental Engineering from the University of Texas at Austin. He is associated with the Environmental Consulting firm of Fred C. Hart, as manager of the Air Quality and Environmental Engineering Group, concerned with fugitive emission sources which are coming under tighter regulatory control. This regulatory control initiative requires that plant managers and employees must be aware of the characteristics of fugitive emission sources. His paper provides information and data dealing with the rapid detection of hydrocarbon leaks. The statistical division of the leaks, which will be used in determining total plant leak rate, and the potential of fugitive emission reduction, due to the aggressive maintenance programs.

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