SOLVENT CLEANING OF PVC REACTORS

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Air Products has chosen solvent cleaning of its PVC reactors as being the most suitable method of completing one step toward the major goal of achieving closed-reactor operation. This mode of operation is one of our major objectives for reduction of employee exposure to, and emissions of, vinyl chloride. This afternoon I will discuss several of the points which were considered in this choice of technologies.

The choice of the most suitable method for accomplishing a given goal usually is based on a balance of a series of cost/benefit decisions for several factors. Seldom, if ever, can a proper decision be made without a detailed appraisal of the particulars of a plant - its equipment, its products, its processes, and its location. No one rule can be made that will be generally applicable across an entire industry.

First, it was necessary to adapt the process to be chosen to existing reactors, either those already in place, or so far along in construction that mechanical changes could not be made. Closed reactor operation with high pressure jets would require the presence of nozzles large enough for the passage of the rotating heads, and these were not available.

In addition, many of the existing reactors were relatively old at the time this decision was made, with extensively damaged inner surfaces. Thus, polymer buildup was rapid, and conventional cleanings would have had to have been quite frequent in order to maintain high quality product. It did not appear from our preliminary evaluation of this techniques that we could maintain the desired quality and still meet the proposed EPA reactor-opening limits, even with an efficient water purge system.

We had made a commitment to the use of reflux condensers in a large part of our operation, and for the sake of both safety and economy, these must be kept free of buildup. We felt that solvent cleaning would be the best method for doing this.

At this point, we surveyed the available technologies, both domestic and foreign, relative to antifouling methods and other clean wall processes, and concluded that even with the assistance received from these systems, we would still need a reactor cleaning method from time-to-time.

Thus, having decided to utilize solvent cleaning, we had to decide on which solvent. A variety of materials was available, and several which have been used or recommended are listed in Table I. These range from poor solvents such as ethylene dichloride, which must be used with high

Table 1. Comparison of cleaning materials.

SOLVENT	MATERIAL COST	SOLVENT POWER	EASE OF RECOVERY	REMARKS
Ethylene Dichloride	Low	Low	High	Toxicity
Ketones	Low	Medium	Medium	Volatility
DMF	Medium	High	Medium	Potential corrosion
Tetrahydrofuran	High	High	Medium	Peroxides, volatility
NMP	High	High	Very low	Very difficult to recover

frequency before the buildup becomes very thick, but which can be recovered very simply and quickly, through the ketones which are intermediate in solvent strength to the very good solvents such as tetrahydrofuran, methyl pyrrolidone, and dimethyl formamide. These latter materials are quite good solvents, and can remove very heavy buildup under the proper conditions.

After consideration of the type of polymer deposits we expected to see in the future, the type of equipment we intended to build, and our own experiences, we chose dimethyl formamide. One important factor in this decision was that we manufacture this material and therefore are familiar with its characteristics. Just as those who manufacture vinyl chloride and are familiar with ethylene dichloride have chose it for their reactor cleaning solvent, and even for the end of the pipe abatement scrubber in place of an incinerator, we felt more comfortable committing our resources to develop a process using a familiar material.

Another important factor was its good solvent power. We manufacture substantial quantities of acetate copolymer, and this system is subject to occasional partial or complete failures of the suspending system, which can result in severe fouling, or even in a phenomenon known as a "set-up". We felt we needed the availability of a strong solvent as we moved toward the manufacture of these products in 24,000 gallon vessels.

We therefore began development of a process to utilize this solvent. The actual reactor cleaning operation is simple. When a reactor is to be cleaned, the residual vinyl chloride vapor is displaced by the water purge system, and the water is displaced with an atmosphere rich enough in nitrogen to avoid the possibility of explosive mixtures in subsequent operations. The reactor is filled to overflowing with the solvent, the vapor being displaced to the storage tank, and the reactor is heated and stirred for the required time. A small flow of solvent is maintained in order to sweep the reflux condenser with warm solvent through the cycle. The solvent is then returned to the storage tank, and the reactor rinsed with water. The first rinse is directed to a solvent-rich storage sump of gradual release to the biological treatment system. The reactor is then ready for evacuation and recharge.

The solvent regeneration system is more complicated. The point at which regeneration is needed is an economic balance between recovery cost and cleaning time. Both the accumulated solids and the water concentration are a factor in the solvent power. Thus the regeneration is done so as to maximize the overall efficiency, bearing in mind the type of wall deposits that are being removed.

Figure 1 is a drawing from U.S. Patent 4,009,048, which describes our process. Spent solvent is mixed in precipitation tank 21 with recycle water of suitable temperature. The flocculated solids are separated in a centrifuge, reslurried in tank 37 to remove entrained solvent, recentrifuged, and sent to disposal. The organic phase is flashed to reduce the acid content and distilled to separate the solvent and water.

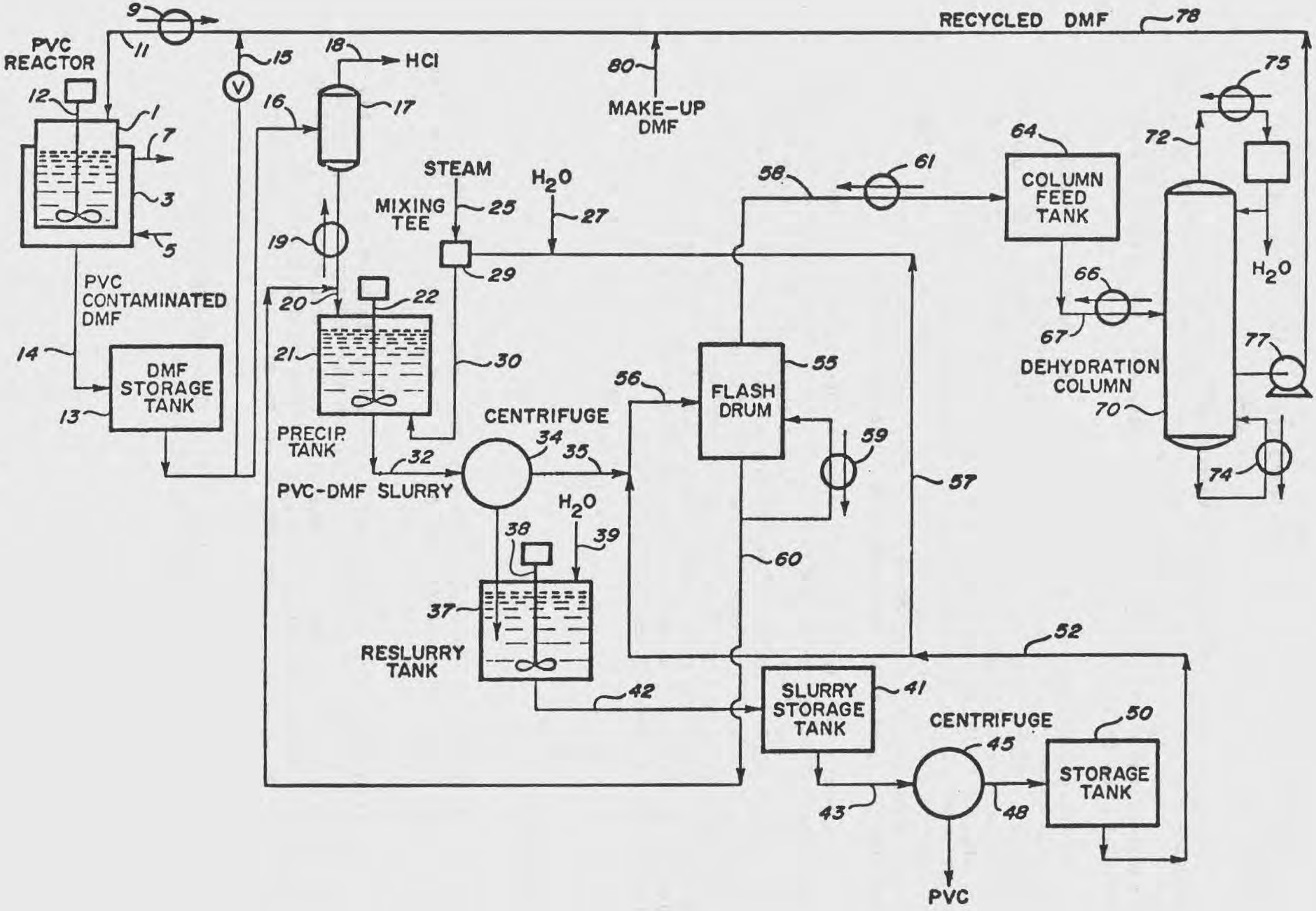
RECYCLED DMF
78
9
11
PVC REACTOR
12
1
7
3
5
15
V
18
HCl
16
17
80
MAKE-UP DMF
64
COLUMN FEED TANK
75
72
H$_2$O
STEAM
H$_2$O
MIXING TEE
25
27
29
58
61
19
20
22
21
30
PVC CONTAMINATED DMF
14
DMF STORAGE TANK
13
PRECIP. TANK
32
PVC-DMF SLURRY
CENTRIFUGE
34
35
56
FLASH DRUM
55
59
57
66
67
DEHYDRATION COLUMN
70
77
74
38
H$_2$O
39
37
RESLURRY TANK
60
52
42
SLURRY STORAGE TANK
41
CENTRIFUGE
45
50
STORAGE TANK
43
48
PVC

FIGURE 1

The system is now in operation in our plants manufacturing both homopolymer and copolymer, and has found application in our emulsion operations.

Commercialization has not been without difficulties. The formate-chloride combination can lead to severe corrosion problems if not handled properly. Copolymer precipitates are more difficult to process because of their more tacky nature. Nevertheless, the system is now operating successfully in our plants.

One by-product of this technology, above the goals of reduced employee exposures and emissions, has been improved life of our equipment. Reactor manways are no longer damaged from frequent openings and contact with ladders, tools and buckets, and interior surfaces are not subject to mechanical harm. One glass-lined reactor that is over eight years old and has been cleaned only by solvents still has a near-perfect glass surface, and thus fouls at a much slower rate than others that have been mechanically cleaned. Polished stainless steel surfaces are similarly protected from mechanical damage.

In summary, we have found that many factors must be considered before the "right" process can be chosen. It is the accomplishment of the end goal that is important in the long run and the means of achieving that goal should be left to the ingenuity and capability of the individual companies. This will ensure that most satisfactory solution for each situation, and provide a diversity of technology for the future. The successful development and commercialization of this process is an example of just such a result, which would not have occurred if technology had been frozen by regulation.

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DISCUSSION:

MR. D. G. IRWIN: Mr. Krause, you listed several ways of improving your reactor design, reducing the fouling. Can you tell me which was the most effective?

MR. FRED KRAUSE: I am not sure I can really state which is exactly the most effective. It is fairly obvious in the industry if you looked into a PVC reactor, or any place where there is a stagnant spot, fouling will build up and continue to build up in subsequent polymerizations. Minimizing those points in the reactor is the only way to reduce that buildup.

MR. IRWIN: You had to complete all of these things to be as effective as you were in eliminating buildup?

MR. KRAUSE: Yes. Eliminating buildup is a combination of things. It is not strictly one thing, as anybody in the industry who is familiar with it knows.

MR. ARTHUR SPIEGELMAN: I would just like to make a comment. Both Fred Krause and John Barr have show us two ways in which to apply control technology without changing the materials involved, and without putting greater stress on instrumentation and things of that naure, and I think that I can show you a few other ways when I get up to speak, but I think it is very important for us to realize that the design of the equipment and the method of operation are just as important, from a control technology standpoint, as examination of the original raw materials.

MR. R. NICHOLAS WHEELER: Mr. Krause, I am a little bit curious as to whether this particular chemical procedure would be adaptable to other monomers?

MR. KRAUSE: We have, obviously, looked at that. I think it is very important as to what the chemical nature of the product is and the chemical of the coating in general. It is not applicable to other products.

MR. WHEELER: I thought it might be a little bit specialized.

MR. JAMES A. GIDEON: Would either of you care to comment on what additional options you have open if you were putting in a new polymerization line, over and beyond those which are available for existing lines?

MR. KRAUSE: John and I will both comment a little on that. We're not going to say too much, because be both have installed new plants within the last several years. Sure, we have taken advantage of everything we could.

We use these coatings to minimize reactor fouling, and as I said, it is part and parcel of the total technology when you design these systems to do that. This is on the edge of properietary information and I don't think we are going to say much more than that. There are obviously things that can be done.

MR. JOHN T. BARR: I agree entirely with what Fred says. The two methods we have discussed here are not mutually incompatible. If you have a workable anti-fouling system, we use the solvent less frequently. The kind of plant you build and the kind of products you build are dictated by the market, and these are not necessarily totally interchangeable.

MR. DONATO R. TELESCA: Fred Krause will now come back and talk to us about monomer stripping. Reduction in monomer content reduces worker exposure in the PVC production operations. This technology is currently commercialized in the United States and licensed to a number of PVC producers world-wide, and I am sure it is available to license to others that may be interested.

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Held at the
Atlanta Hilton Hotel
Atlanta, Georgia

February 27-28, 1979

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Physical Sciences and Engineering
Cincinnati, Ohio 45226

January 1981

For sale by the Superintendent of Documents, U.S. Government
Printing Office, Washington, D.C. 20402

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DHHS (NIOSH) Publication No. 81-107