

SPECIALTY VINYL CHLORIDE RESIN PROCESSES

EFFECTS OF GOVERNMENTAL REGULATIONS

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Specialty vinyl chloride resins are a small segment of the total PVC industry, but they are a very important segment. The addition of vinyl chloride either as PVC or as a segment in the resin molecule imparts qualities of toughness, wear resistance and water resistance to coating materials. For this reason the specialty resins are found in a variety of PVC coatings such as organ sols, lacquers, powder coatings and latexes. In addition to coatings made up wholly of PVC resins, they also are widely used to modify and improve other coating systems such as alkyd, epoxy, nitrocellulose, phenolics, polyurethane and polyesters. Two of the most visible examples of vinyl coating systems are the beer can and the Golden Gate Bridge. There are other uses for the specialty resins where their formulating latitude, their low extractibles, their ease of fabrication and their low vinyl chloride monomer content make them very valuable. Surgical devices are excellent examples of this use.

The specialty vinyl resin processes are shown on Table I.

TABLE I

	<u>Percent of Total PVC Industry</u>
Solution Polymerization	3%
Latex Polymerization	1%
Continuous Bulk Polymerization	0.5%
Total	4.5 %

Response to governmental regulations, the OSHA vinyl chloride standard primarily, looks like the simple five-step program shown on Table II.

TABLE II

ACTION PROGRAM FOR GOVERNMENTAL REGULATION

1. Interpret regulation
2. Define the problems
3. Act on the problems
4. Evaluate results of action
5. Repeat steps 1 through 5

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This action program is nothing more than the classical approach to the trial-and-error solution of a complex mathematical problem - an equation that when you plug in zero for the answer every other factor in the equation becomes infinite. The objective of the various governmental vinyl chloride regulations is to produce a zero exposure; however, the government too is concerned that the expense factors will become infinite. Thus, you have the current and proposed regulations that require less than one ppm, best available technology or non-detectable.

In the specialty vinyl chloride resin processes interpretation of the regulations is very important for three reasons. First, because the drafters of the regulations based their work on the processes and resin applications that make up the other 95% of the industry. Second, because no matter how clear and specific the regulation sounds on first reading it becomes increasingly vague and difficult as you try to apply it to the processes at hand - specialty vinyl resins. Third, because the objective of the regulation suddenly gets lost in the mechanics of compliance. For example, the current OSHA vinyl chloride standard based upon suspension vinyl resins containing 1,000 ppm of residual monomer covered all operations until the resin became a "fabricated product". The objective was to protect all workers from excessive exposure to vinyl chloride in calendering, molding and extrusion plants using the suspension resins. These large plants were not too difficult to identify and control. The specialty vinyl resin business unfortunately did not fit this concept, the resins and latexes had residual vinyl chloride monomer contents ranging from ten ppm to nil. They were marketed to literally thousands of customers in small quantities. They were also competing with non-vinyl chloride materials in coating and adhesive applications. Faced with trucking companies and customers who wanted to avoid employee hazards, who did not want to be burdened with the extra cost of the vinyl chloride regulation and who did not have to use or transport the vinyl chloride resin, the industry was on the road to extinction. The problem was discussed with OSHA and with their counsel the industry set out to show the inherent safety of these products in use. Their low VCM content resulted in little or no work space air contamination during use. This documentation was accepted by OSHA because it clearly showed that the standard's objective, employee protection, was being met. As a result, these materials were classified "fabricated products", i.e. materials which on further processing did not release sufficient vinyl chloride to cause the work space air concentration to exceed the action level (0.5 ppm). The classification exempts the transporter and user from the standard's regulations but not the manufacturer of the product. This case shows the value of cooperative industry/government effort as opposed to the adversary approach between government and industry which seldom settles anything.

For the specialty vinyl resin processes the definition of problems and evaluation of action results were dependent upon methods of analysis, analytical equipment and trained analytical personnel. Analytical work in this area is more difficult and more prone to error than suspension PVC homopolymer manufacture due to

the variety of materials. Of particular difficulty was the presence of acetaldehyde, a hydrolysis product of vinyl acetate. When the gas chromatograph column was inadequate or the equipment was not performing properly, acetaldehyde was counted as vinyl chloride. Sometimes the error was obvious and other times it was not. Solvents in the samples slowed the analysis rate through the need for long purging periods for the chromatograph column. These problems were corrected by use of long columns and reverse flushing the section of the column where the solvents collected.

Good analytical methods are of no help unless the samples are taken often and the results are timely. For example, an initial program of air sampling and analysis was undertaken in a resin operation. The program involved repetitive samples of 29 points within the plant with the analytical results available one to two days later. Based on this program the plant had an average VCM concentration of 10.2 ppm with 95% of the analyses less than 46 ppm. This appeared to be a good performance in the early days but the data delivered two days later was of no value in establishing control of emissions. An automatic chromatograph was installed to give immediate results so that corrective action could be taken promptly. The automatic analyzer yielded some startling results. The average concentration of VCM was 16.3 ppm not 10.2 ppm and 10% of the analyses were over 50 ppm, the then current standard. When the OSHA standard was reduced further to one ppm TWA the automatic monitors became even more valuable in providing timely data so proper corrective action could be taken.

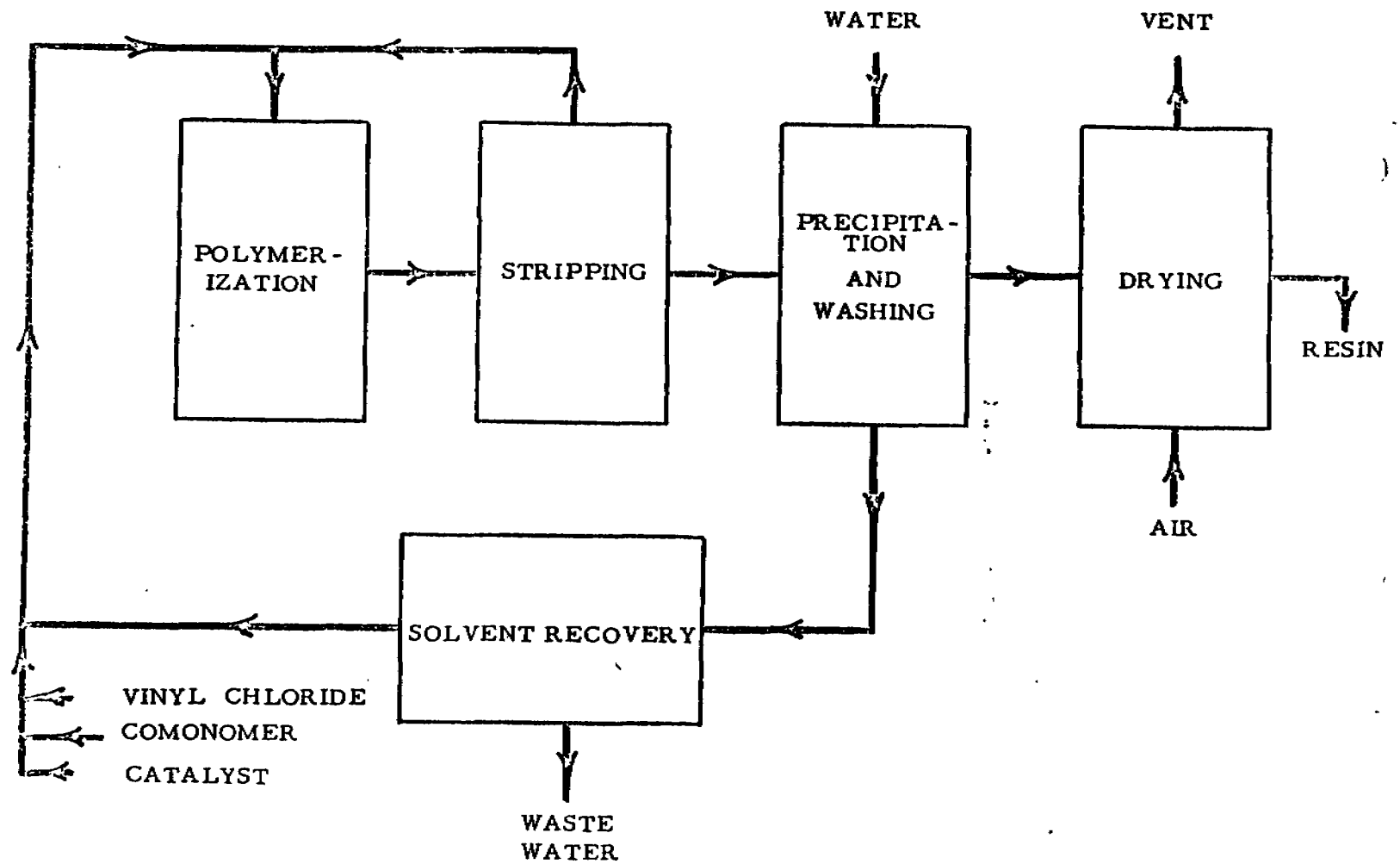
Understanding, acceptance, and commitment are words that characterize the people portion of this effort to meet governmental regulations. When everyone involved in the plant clearly understands the regulation and the problems related to it, accepts his responsibility for doing his part and is committed to the necessary goals, then progress is made. This people resource and its proper utilization had a major effect on the speed with which the regulations were met in many cases at minimum cost. It has been used to good advantage in the specialty vinyl resin area from laborer to plant manager.

The last important general factor in vinyl chloride control was the almost unlimited availability of corporate technical and financial resources. The specialty vinyl chloride resin industry's progress in VCM control was limited solely by equipment deliveries and lack of viable data on problems. Corporate management too was wholly committed to worker and public protection.

SOLUTION POLYMERIZATION

The solution polymerization process is the oldest vinyl resin process practiced in the United States and the most capital intensive. The flow diagram (Figure I) shows the major process steps. Vinyl chloride, comonomers and peroxide catalyst are mixed with a solvent and polymerized continuously to form a clear, syrupy resin solution. The reactor product is stripped of its unconverted

FIGURE I
SOLVENT VINYL RESIN PROCESS



monomer. The monomer-free resin solution is then treated with water to form solid resin particles. The solvent and water are separated from the resin and the resin is dried and packaged. The solvent is recovered and reused. The advantages of the process are obvious. The polymerizers are continuous and non-fouling. The unconverted vinyl chloride can be essentially completely removed. The resin product is free of electrolytes, soap, suspending agents and other extractible materials. The disadvantages are that the resin produced must be soluble in the solvent. (This limits the product to resins containing a maximum of 91% vinyl chloride and inherent viscosities of 0.75 or lower). Manufacturing cost is higher than other processes due to extra processing steps, higher energy usage and solvent losses. The higher manufacturing cost and composition limit these resins to areas such as clear sheeting and solution coating where its superior properties justify its higher cost. In product application the process limitation that the resin must be soluble in the processing solvent becomes an advantage. The resins are soluble in a wide variety of solvent systems and compatible with a wide variety of coating materials. They can thus give the coating formulator a wide latitude in preparing tough, flexible coatings whether it be for tooth paste tubes or ship bottoms.

The safety and EPA regulations are not as difficult to meet with the solution process as with the suspension or emulsion polymerization processes because of its nature. There are, however, problems to be overcome. Table III shows personnel exposure to vinyl chloride in 1974 as well as the present exposure levels. As you can see the level of exposure is under good control.

TABLE III
SOLVENT RESINS VCM EXPOSURE
(Eight Hour TWA)

<u>Operator</u>	<u>1974</u> <u>ppm</u>	<u>1976</u> <u>ppm</u>
Number 1	40	0.3
Number 2	10	0.2
Number 3	5	0.2
Number 4	5	0.1
Number 5	1	0.0
Number 6	<1	<0.1

Table IV shows vinyl chloride emissions to the air for a typical solution polymerization plant in 1974 and 1976 in terms of pounds per 1,000 pounds of product. The reduction in emissions shown here are the result of the OSHA standard. To obtain less than one ppm VCM in the work space air emissions from the process had to be reduced.

TABLE IV
SOLVENT PROCESS VCM EMISSIONS
(Pounds/1,000 Pounds Product)

	1974 <u>Lbs./M</u>	1976 <u>Lbs./M</u>
Reactor Operations	0.18	0.08
Monomer System Vent	0.07	0.000
Product Stripper	12.47	0.003
Equipment Maintenance	0.04	0.04
Leaks	0.25	0.000
Total Emissions	13.01	0.123

Comparing the present air emissions with the proposed EPA emission standard (Table V) shows that the solvent polymerization process emits 30% of the total permitted by the EPA for a suspension PVC plant. EPA, however, does not accept overall performance but insists upon specific control technology. To comply with the proposed EPA standard, the solvent polymerization process will therefore be permitted to emit only 0.017 pounds VCM per thousand pounds of product, less than 5% of that permitted by a suspension resin plant.

TABLE V
SOLVENT PROCESS VCM EMISSIONS
(Pounds/1,000 Pounds Product)

	1976 <u>Lbs./M</u>	Proposed EPA Standard <u>Lbs./M</u>
Reactor Operations	0.08	0.01
Monomer System Vent	0	0.000
Product Stripper	0.003	0.40
Equipment Maintenance	0.04	0.004
Leaks	0.000	0
Total Emissions	0.123	0.414

Returning to (Figure 1) the flow sheet the major items leading to the performance shown are:

1. Reduction of the number of reactor control samples cut air emissions by 0.1 pound per 1,000 pounds of product. This was accomplished by the use of in line continuous analyzers.
2. Reactor operator exposure was cut by the elimination of reactor sampling and by pressure ventilation of the control area. Ventilation at one air change every two minutes was ineffective if there was any measureable emission. Location of the intake is critical. On occasion more VCM came in the intake than was emitted in the building.
3. The monomer recovery system vent was cut from 0.07 pound per 1,000 pounds of product to nil by incinerating the vent in the steam power plant. The emission of hydrogen chloride from this operation is negligible compared to the gases generated by coal burning.
4. Emission from the system downstream of the stripper was cut from 12.47 pounds to 0.003 pounds per 1,000 pounds of product by doubling the number of stripping stages and precise control of stripping. This change essentially eliminated vinyl chloride monomer exposure and air emissions downstream of the monomer recovery operation.
5. Major identifiable leaks were confined to reactor agitator packing glands. These were essentially eliminated by installation of mechanical seals.

Major items that remain to be done assuming that the proposed EPA standard is promulgated as proposed are:

1. Reduce reactor operations emissions from 0.08 to 0.01 pounds per 1,000 pounds of product. This is a maintenance emission whose final disposition is not believed to be difficult. At least once a month reactors are solvent washed to clean cooling coils. During this washing some VCM is emitted to the air.
2. Emissions caused by equipment maintenance must be reduced from 0.04 to 0.004 pounds per 1,000 pounds of product. This can be achieved by using portable compressors to evacuate the equipment if one can be found that is acceptable to EPA. The proposed EPA standard is as stringent for small compressors used intermittently as it is for a major process compressor in continuous service. Small compressors simply lack the sophisticated packing systems required by the proposed EPA standard.

3. Revision of reciprocating pump and compressor packing glands or replacement with rotary machines. In my opinion the emission reduction here will be negligible. In addition, the proposed EPA standard for these items is not clear; therefore, the nature of the problem and its ultimate solution are in limbo pending further direction from EPA in its promulgated standard.

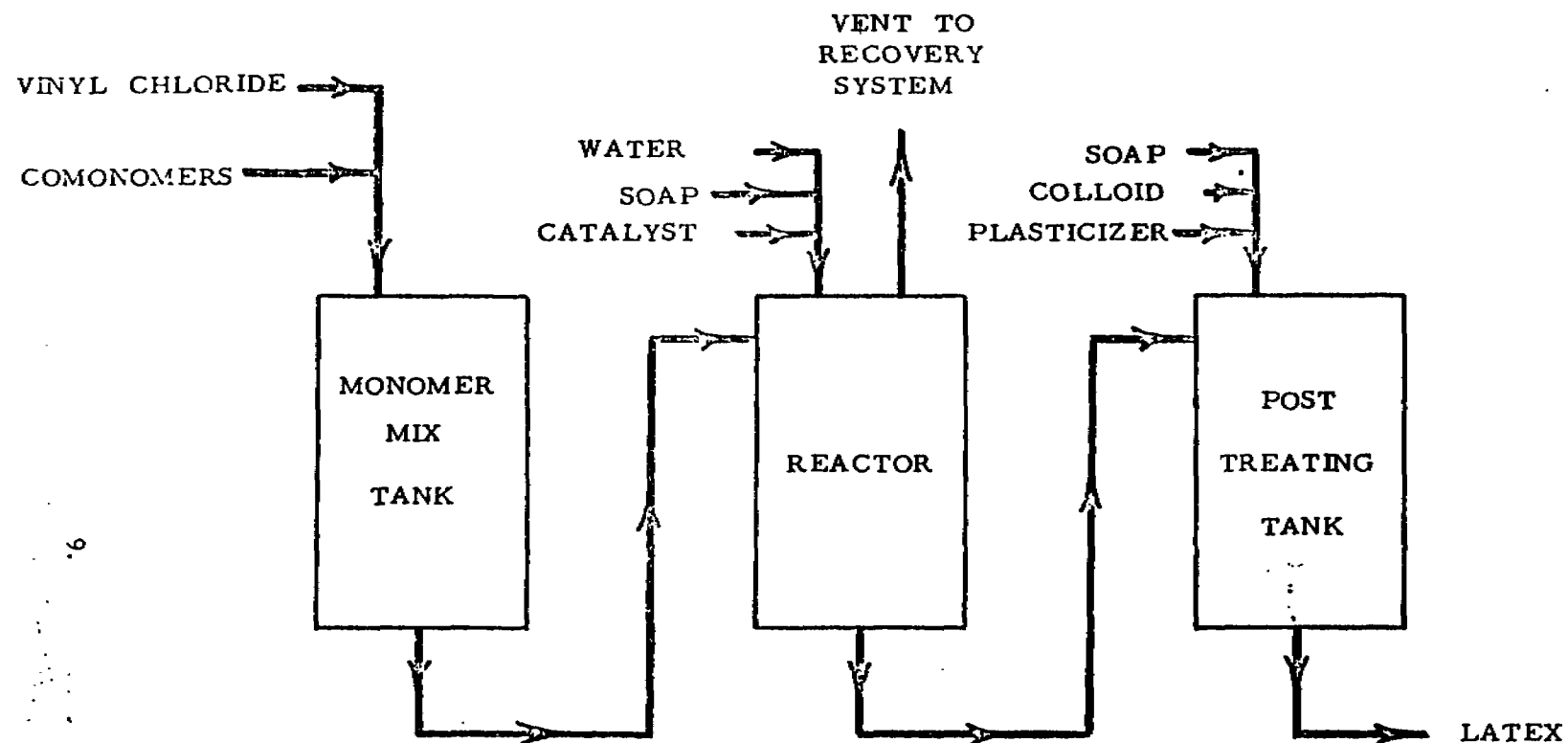
In the interest of brevity many changes and problems have not been discussed. Nevertheless they were defined and corrected. Taken as a whole the solution polymerization process for vinyl resins probably has the lowest employee exposure, the lowest emissions to the air and produces the cleanest resin of any vinyl chloride resin process known.

LATEX POLYMERIZATION

Latex polymerization processes are one of the most rapidly growing business areas in the coatings field. This comes from environmental pressure to reduce emissions of solvents by coating applicators to the atmosphere. Latex technology has made great strides in recent years to provide coating materials for markets where they had been previously excluded due to unsatisfactory performance. Latex plants are small when compared to a 100MM pound suspension PVC plant. The flow diagram (Figure II) shows the major process steps. The latex polymerization could probably be termed batch continuous in that water and surfactant are charged to the polymerizer along with a small amount of the monomer mixture. Catalyst and monomer mix are then fed continuously until the latex has reached the targeted resin content and the reactor is essentially full. From reaction start to the end of the polymerization the time is three to five hours. The reacted latex batch is then modified by additions of soap, colloid, plasticizer and a post polymerization catalyst. Use of post polymerization catalyst addition results in further polymerization of the residual monomer in the latex. The ultimate residual monomer concentration is a function of time and the amount of post polymerization catalyst added. The finished latex product is usually shipped by tank truck to a coating or paint manufacturer or for industrial coating applications it may go directly to the coater. There are other techniques for latex manufacture in use but in the interest of simplicity these are not discussed. The vinyl chloride control problems do not differ appreciably regardless of the manufacturing technique.

Regulatory problems unique to latex operations stem from the use of small multi-use facilities for manufacture and the wide variety of latex applications.

A typical latex plant, whether separate or a part of a larger resin plant makes a variety of products. For purposes of this discussion only a fraction of the products contain vinyl chloride. Latex plants are usually matched with local markets. Long distance shipments are avoided because the freight penalty from shipping large amounts of water makes the local plant more profitable. There is no such thing as a typical plant product mix.



VINYL CHLORIDE LATEX PROCESS

FIGURE II

Meeting the OSHA standard for exposure to vinyl chloride is a difficult though fairly straight-forward problem. OSHA merely requires that the permissible exposure limits be met. It does not specify how they are to be achieved. The progress toward meeting the OSHA standard in our typical latex plant is shown in Table VI.

TABLE VI
VCM CONTENT OF LATEX PLANT WORK SPACE AIR

	<u>Year</u> <u>1974</u>	<u>Year</u> <u>1976</u>
Monomer Unloading	200 ppm	5 ppm
Reactor Area	2 ppm	<1 ppm
Filtration Area	1 ppm	<1 ppm
Product Area	<1 ppm	<1 ppm

The OSHA standard also resulted in decreased air emissions of vinyl chloride. Since work space air and ambient air are often the same, control of one tends to control the other. These reductions are shown by Table VII.

TABLE VII
VINYL CHLORIDE BALANCE FOR LATEX PRODUCTION

	<u>Year</u> <u>1974</u>	<u>Year</u> <u>1976</u>
Product (PVC) Pounds	95.43	98.48
Product (VCM) Pounds	0.30	0.00
Waste (PVC) Pounds	0.05	0.05
Loss (VCM) Pounds	4.22	0.03
Incinerator (VCM) Pounds	0	1.44
Monomer Input (VCM) Pounds	100.00	100.00
(VCM) Loss Lb. /M Lbs. Solids	10.45	0.97

The effect of the proposed EPA emission standard for vinyl chloride cannot be forecast since certain areas of the standard are not clear. Many of the emissions controlled by the proposed EPA standard have been changed as a result of the OSHA standard. In addition, the application of a standard based upon a large suspension or dispersion PVC resin plant to a relatively small multi-purpose facility is going to require considerable interpretation. For example, is the product, the gross plant output, the products containing vinyl chloride or the vinyl chloride actually contained in the polymer? How does the VCM limit on stripped product apply to a plant with no stripper? Does the standard apply only during PVC latex manufacture? When EPA issues its VCM emission standard then the problems of equivalency and interpretation will be worked out.

The process flow sheet (Figure II) serves best to describe the major actions leading to the changes in performance:

1. Reduction of residual monomer contained in the product was for reasons discussed previously a prime objective. Fortunately, the procedure of using post reaction catalyst additions was in use for other latexes. Thus, the problem was largely one of selecting a proper catalyst and establishing the operating procedure. The results are shown in Table VIII.

TABLE VIII
RESIDUAL VCM CONTENT OF PVC LATEX

	<u>Year</u> <u>1974</u>	<u>Year</u> <u>1976</u>
Latex A	600 ppm	3 ppm
Latex B	300 ppm	2 ppm
Latex C	60 ppm	2 ppm

A side effect of this reduction was lowered work space air concentrations of VCM downstream of the reactor; thus, the control area was reduced to equipment used for reaction and raw material storage.

2. Incineration of reactor and tank vents provided for control of VCM emissions from the reaction and storage areas. Obtaining adequate natural gas and disposition of the hydrogen chloride formed are continuing problems.

3. Reactor product changecovers were made without equipment cleanup; thus, any VCM contained in the reactor was reacted into a non-PVC latex. This technique requires careful study and product selection to maintain overall product quality.
4. Emissions during monomer unloading were reduced by inert gas purging of the unloading hoses to the supplier's truck and using dry disconnect couplings. These couplings contain check valves that close automatically when the hose is disconnected; thus, the VCM is held in the hose rather than emitted to the air. This is a feasible solution when small hoses can be used.

Items which are troublesome under the OSHA standard and will be affected by the proposed EPA standard are:

1. All rotary pumps handling VCM or mixtures of VCM will have to be equipped with double mechanical seals instead of their present single seals. No measureable change in VCM emissions is expected though, theoretically, emissions caused by seal failure are lower with double seals.
2. Revision of reciprocating compressor and pump packing glands in a manner acceptable to EPA. As mentioned earlier, this portion of the proposed EPA standard is unclear. No measureable change in emissions is expected.
3. VCM emissions caused by control of equipment maintenance for items in monomer service is awaiting promulgation of the EPA standard. Since only the monomer storage tank and piping are involved, the investment will be minimal.

The effect of the VCM health and air emission regulations on latex plants has been to tax the engineers ingenuity to the utmost. Many of the controls used make full utilization of available facilities and knowledge. This is one advantage of the program discussed earlier in that investment for control equipment is optimized.

CONTINUOUS BULK POLYMERIZATION

Continuous bulk polymerization of vinyl chloride produces a fine, very porous resin particle containing no surfactants, suspending aids or other extractible material. The porous fine particle gives up residual vinyl chloride monomer very readily; thus, these resins as sold contain 0 to 10 ppm vinyl chloride monomer. The resins find use in plastisols, slush and powder coatings and in medical devices such as blood bags.

The flow diagram (Figure III) shows four steps: polymerization, monomer stripping, dewatering and drying. The process operates on the principle that polyvinyl chloride is insoluble in vinyl chloride. Vinyl chloride, catalyst and comonomer are fed to an agitated reactor; as the monomer polymerizes the polymer precipitates so that the reaction mass is a slurry of resin suspended in monomer. Some heat of reaction is removed by jacket cooling, but most is removed by evaporation of monomer. Resin slurry is removed to the stripper where it contacts hot water driving off the unconverted monomer and yielding a resin water slurry. This is vacuum stripped to remove more monomer. The resin is dewatered and dried in an air drier.

The major problem contributing to emissions is equipment fouling with resin deposits. These deposits must be removed manually from the reactor and accessory pipelines. Reactor cleaning is required about every five days.

The continuous bulk polymerization is relatively old in terms of technology and plant. The fact that it is still operating is indicative of the unique properties of its resins. Age has, however, not prevented progress toward meeting the current and proposed regulations. Table IX shows the change in personal exposure from 1973 to 1976.

TABLE IX
CONTINUOUS BULK PVC PERSONAL VCM EXPOSURE

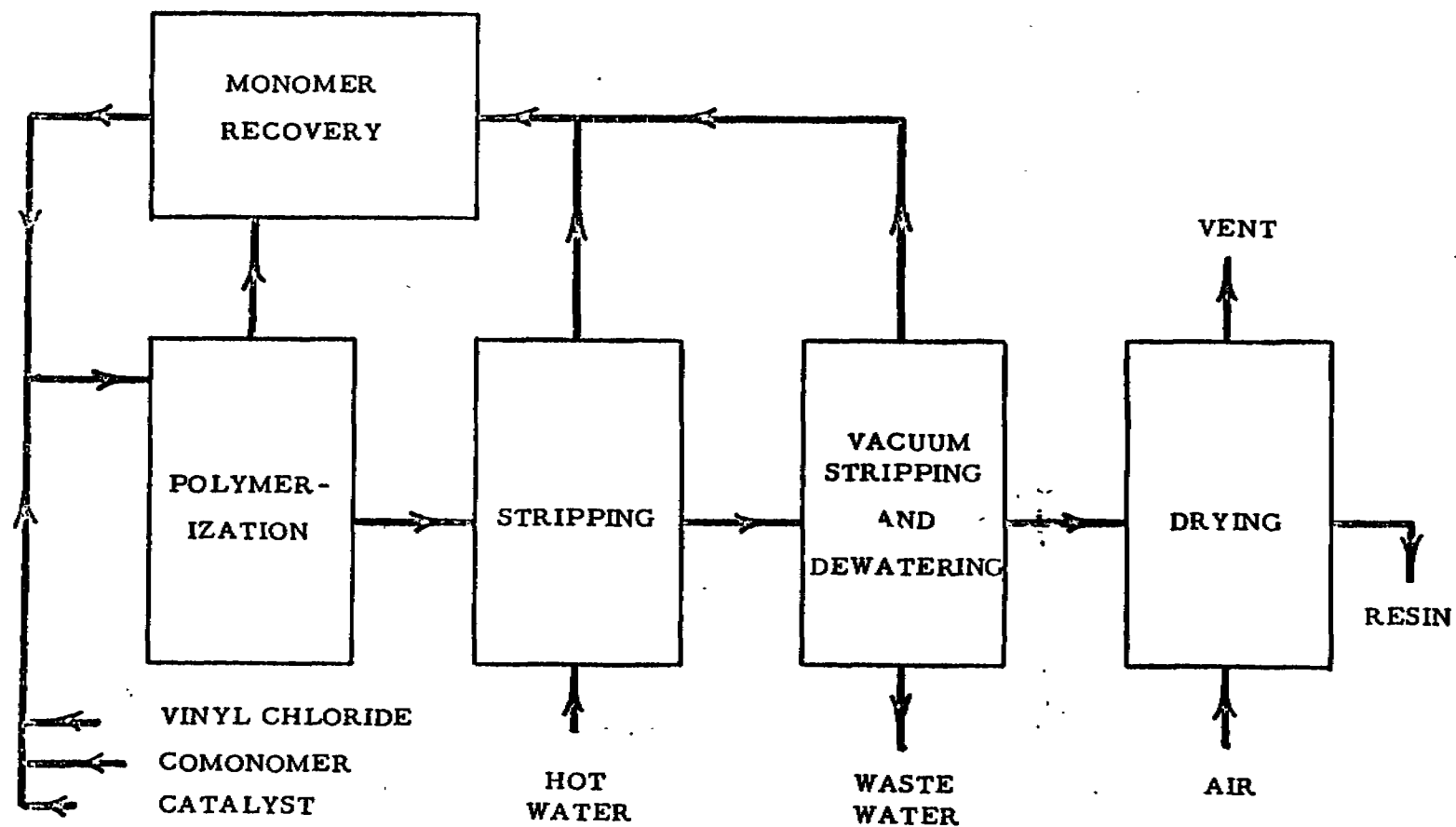
<u>Operator</u>	<u>Year 1973</u>	<u>Year 1976</u>
Number 1	7.9 ppm	0.5 ppm
Number 2	3.6 ppm	0.05 ppm
Number 3	7.95 ppm	0.43 ppm
Number 4	2.4 ppm	0.14 ppm
Number 5	16.6 ppm	0.14 ppm

The low TWA exposures for 1976 raise a question. The OSHA standard states that TWA exposures of less than 0.5 ppm require no control action yet on the day these measurements were made four out of the five men wore a respirator for a part of the day. The plant, as a safety policy, chooses to avoid employee exposure if there is a possibility of an emission.

The continuous bulk polymerization plant is a part of a larger suspension resin operation; therefore, no specific data on ambient air emissions is available.

Operational changes caused by the regulations are as follows:

FIGURE III
CONTINUOUS BULK VINYL RESIN PROCESS



14.

1. Solvent scrubbing of the monomer recovery system vent reduced the VCM concentration of this stream to less than 0.5%. The vent from this system was then incinerated in the local steam power plant. The solvent scrubbing system operates at 100 psi cleaning 400 pounds of vent gas per hour with methyl ethyl ketone.
2. The process control rooms where the operators spend most of their time were pressurized and ventilated with air from a remote location. When an operator has to go to a particular plant location he checks the VCM monitor and uses a respirator if the need is indicated.
3. All rotary pumps in vinyl chloride service were equipped with double mechanical seals as required by the proposed EPA standard. In this plant there was a decrease in the work space air concentration as a result of the change from packing and single seals to double seals.

Process development and new investment remain to be done in this process to achieve full compliance with the OSHA standard and the proposed EPA standard. Major items for further work are:

1. Improved resin slurry stripping. The present two-stage continuous system is barely meeting the minimum EPA limit for stripping. The monomer left in the very porous resin particle readily leaves the resin in the drier; thus, the resin leaves the process in the 0 to 10 ppm RVCM range. Improved stripping would reduce the dried resin to 0 ppm RVCM and would reduce potential employee VCM exposure in the drying area. The number of stripping stages and operating conditions are not yet fully determined.
2. Improved monomer recovery. Replacement of the existing reciprocating compressors with rotary units is in the engineering stage. This change will be a part of an overall revision of the recovered monomer system to provide more surge capacity, to reduce safety hazards caused by vacuum operation, to reduce vinyl chloride emissions and to reduce the energy requirements of the process. This low conversion process has a major portion of its investment in monomer recovery and handling equipment; thus, this could be said to be a large project.
3. Reactor agitator stuffing box revision. The proposed EPA standard requires that agitator packing consist of double mechanical seals with a pressurized sealing fluid between the seals. Since the reacting material has the potential for complete conversion