

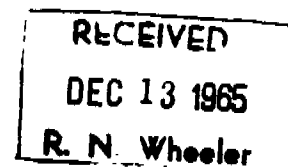
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UNION CARBIDE CORPORATION
Plastics Division

Texas City, Texas

December 7, 1965

TO: See Attached List



SUBJECT: Mild Caustic Scrubbing of Vinyl Chloride Monomer Before Use
in Solvent Vinyl Reactions

The attached report by Mr. T. L. Rapp summarizes the advantages that have been realized in the production of solvent vinyl resins at Texas City by the removal of HCl from vinyl chloride monomer.

Certainly the maintenance cost savings resulting from the use of acid-free monomer are significant but the main advantage, the improvement in resin solution color properties, has been truly impressive.

M. E. Eisenhower
M. E. Eisenhower

MEE/vt

Attachment

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MILD CAUSTIC SCRUBBING OF VINYL CHLORIDE

MONOMER BEFORE USE IN SOLVENT

VINYL REACTIONS

Written by: Thomas L. Rapp

Reviewed by: M. E. Eisenhour

UNION CARBIDE CORPORATION

PLASTICS DIVISION

TEXAS CITY, TEXAS

December 1, 1965

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SUMMARY

Scrubbing of refined vinyl chloride with a mild caustic solution has accomplished the following at the Texas City Solvent Vinyl Resins Unit:

1. All producing systems now yield excellent color resins. This has eliminated several scheduling problems and has improved unit operating flexibility in monomer usage.
2. Acid attack of autoclave feed transfer and metering systems is no longer an operating problem. This has resulted in annual maintenance savings of \$3,000.
3. Acid attack of the autoclave lead lining has been reduced, yielding a corresponding reduction in lead chlorides in the finished resin product. This material, identified as "insoluble white particles" by customers, is a quality degrader; its elimination or reduction is highly desirable.

INTRODUCTION

The production of high clarity solution grade solvent vinyl resins depends to a large extent on the elimination of iron from the feed to the reacting autoclaves. Feed containing above 0.5 ppm iron will generally yield off-color resin. Since iron concentration is so critical, all material handling the autoclave feed is stainless steel or monel. In spite of this, oxides of iron and other insoluble iron compounds remain in the feed system continuously; these, however, are filtered before they enter the autoclave. The only breakdown of this system occurs when hydrochloric acid enters the feed with vinyl chloride. The hydrochloric acid reacts with the iron compounds and changes them into soluble forms which are carried in acetone through the filters and into the autoclaves. Water entering the feed system with the vinyl acetate provides the wetting agent through which the hydrochloric acid becomes most effective. Not only does the system just described affect resin color, but it also affects the life span of piping, motor valves, metering systems, and the such through a slow acid attack.

Resin having poor color properties can be sold only to flooring and record markets. These markets are, however, being rapidly changed over to resin produced by other processes. As a result, disposal of off-color resin is becoming more and more limited, while the necessity for producing high clarity solution grade resin is becoming more and more acute.

Three possible solutions to this problem were considered: (1) Eliminate the iron compounds; (2) Eliminate the water; and (3) Eliminate the hydrochloric acid. The approach chosen as most economical and effective was to eliminate the hydrochloric acid by water scrubbing the incoming vinyl chloride monomer.

DISCUSSION

A check of the literature indicated that hydrochloric acid could be removed from vinyl chloride very effectively by a weak caustic scrubbing. A very small pilot scrubber was built for test purposes. Samples of vinyl chloride were taken before and after scrubbing at three different conditions: Water scrubbing with moderate throughput, mild caustic scrubbing with moderate throughput, and mild caustic scrubbing with rapid throughput. All three methods were 100% effective in removing hydrochloric acid in the 5 - 10 ppm range.

The Plant Corrosion Group advised that the scrubbing solution should not be allowed to become too acid (5.0 pH or lower), or serious attack of stainless steel would result. Since the scrubber tank, piping and other equipment were to be stainless steel, caustic was provided as an additive to the scrubbing liquid mainly as protection against corrosion rather than as an aid to scrubbing efficiency.

A permanent scrubbing system was installed to take a minimum of 15,000 pounds/hour vinyl chloride rate. The tank and circulating pump were already available for this project, allowing the entire system to be installed for about \$2,500. A schematic of the installation is attached. This system was placed in service on June 20, 1964. No difficulty was encountered during start-up or during the first several days of operation.

Two serious problems, possibly related, have developed with this system and have been resolved to an acceptable level. The first of these problems involved excess carry-over of scrubbing liquid to the decanting tank. This problem has been reduced to negligible inconvenience by insulating all equipment and keeping the scrubber contents cold by continuously scrubbing cold vinyl chloride. Although this has eliminated flashing of vinyl chloride which carried considerable water with it, some carry-over continues solely because of the high throughput velocity. The second problem involved the creation of vinyl chloride homopolymer in the scrubber and decanting tanks. This polymer could be removed by filtration, but filter changes became too frequent. This problem has also been considerably reduced by the low temperature operation.

CONCLUSIONS

Since the scrubber has been operating, every blend of resin has passed for solution customer applications on color rating. Scheduling of solution grade production is no longer a problem and unit operating flexibility has been enhanced since all monomer can now be considered as top quality. For numerical comparison, APHA color ratings for two resin types are offered:

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CONCLUSIONS (continued)

	<u>BEFORE</u>			<u>AFTER</u>		
VYHH:	average	-	35	average	-	20
	maximum	-	60	maximum	-	30
VYHK:	average	-	40	average	-	25
	maximum	-	150	maximum	-	40

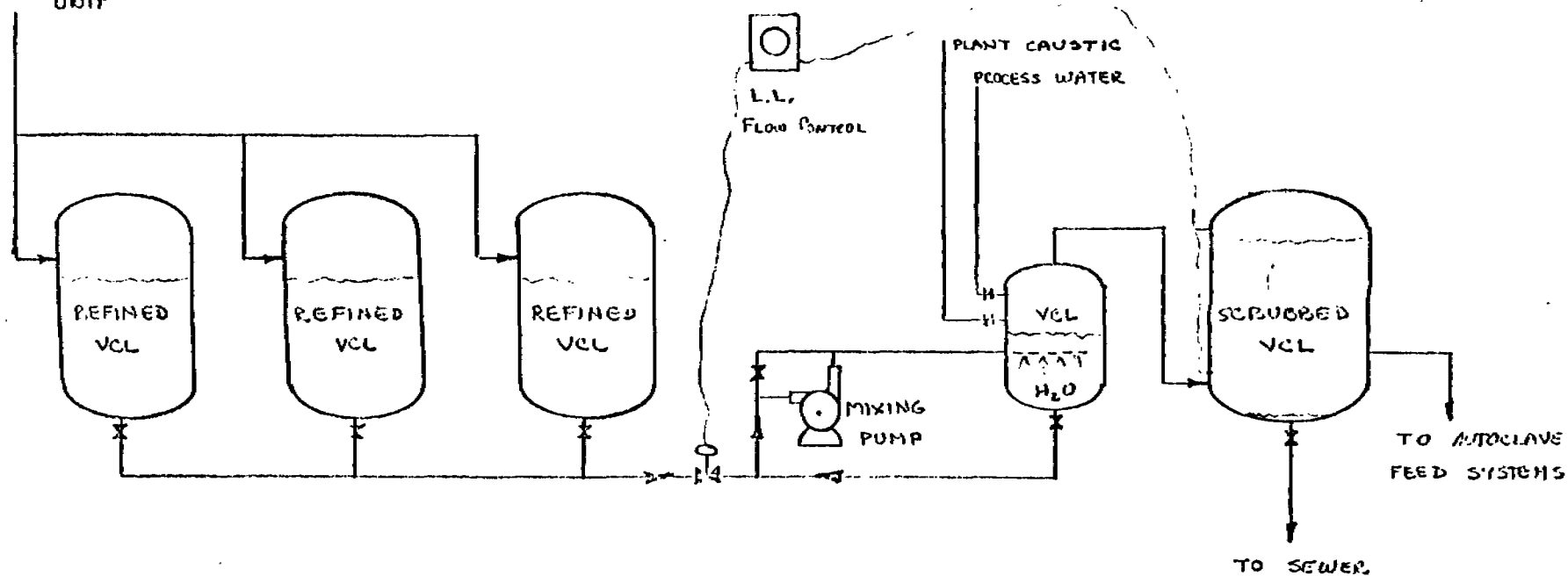
A color rating of 40 is considered to be the highest acceptable for solution grade resin.

Since the scrubbing operation has been in effect, no autoclave feed headers, metering systems, etc., have failed or required overhaul because of corrosion attack. Savings in maintenance labor and material amounts to a minimum of \$3,000 per year.

Elimination of acid has also helped to reduce "autoclave specks". These particles have been identified as lead salts which are formed through acid attack of the autoclave lead lining. Insoluble salts, such as lead chloride, stay in the autoclave varnish and contaminate the final resin product unless removed by a clarification process. An excess of these particles will cause rejection of a blend for solution grade sale. Although this type of contamination is still present, it is significantly reduced since the scrubber has been in service.

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FROM MONOMER
UNIT



VINYL CHLORIDE SCRUBBING

TEXAS CITY ADVENT REFINING UNIT

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