

Depolymerization of Paraformaldehyde

R. E. HALLBECK¹

Formaldehyde in solution is commonly used to control microbiological growth in continuous diffusers. The solid polymer, paraformaldehyde, can be depolymerized and a resultant formaldehyde solution obtained which will serve the same purpose as formalin in the continuous diffusers.

Paraformaldehyde of commerce is a mixture of chain polymers of formaldehyde of high molecular weights (1)². It is a white, crystalline powder. It is only slowly soluble in cold water, but more readily soluble in hot water, with evolution of formaldehyde. Paraformaldehyde is 90 to 95 percent available formaldehyde.

One unit of formaldehyde derived from paraformaldehyde will cost about 57 percent as much as one unit of formaldehyde in formalin, before freight. Costs as delivered to our Spreckels Factory further increases the spread to 50 percent.

It is not desirable to use paraformaldehyde in a solid state directly introduced to the diffuser, though this would seem easiest, because solution and depolymerization of the paraformaldehyde proceed slowly under the conditions generally prevalent in cells of the diffuser when treatment for microbiological control is required. Consequently formaldehyde concentrations, high enough to effect maximum bacteria kill, may not be attained, unless an excess of the bactericide is introduced.

It then is suggested to depolymerize the paraformaldehyde and introduce the resultant formaldehyde solution into the diffuser. Various means were proposed.

According to Peterson (2), the solubility of formaldehyde polymers in water is increased in the presence of methenamine. This was verified for concentrations up to 1 percent of methenamine. Toxicity of this chemical made it unattractive in application.

Depolymerization by vaporization using a jet of steam was considered and discarded since only a trace of moisture will cause polymerization of formaldehyde vapor in the 100° C. temperature range.

Miller (3) holds a patent which provides for generation of pure, monomeric formaldehyde by introducing a suspension of paraformaldehyde in a liquid carrier having a vapor pressure not in excess of 15 mm. Hg. at 200° C. The formaldehyde flashes out leaving the carrier unchanged. Caster oil makes a satisfactory carrier. The process was considered as too elaborate for our requirements.

Paraformaldehyde will depolymerize and go into a 25 percent formaldehyde solution in boiling water in about five minutes with adequate

¹ Chief Chemist, Spreckels Sugar Company, Spreckels, California.

² Numbers in parentheses refer to literature cited.

circulation. At this temperature considerable formaldehyde is lost in vapors. Adequate venting of vapors to prevent discomfort and injury to personnel is a problem. Depolymerization and solution rates fall off rapidly with decreasing temperatures to a point where a 1 percent solution is obtained in 20 minutes at room temperature.

The polymer was reported to be soluble in dilute alkali hydroxide solutions. Experimental work conducted by Spreckels chemists at Woodland showed that at room temperatures the concentration of a formaldehyde solution prepared from paraformaldehyde could be increased from about 1 percent at 8 pH to 22 percent at 12 pH. These monomeric formaldehyde concentrations were reached in 20 minutes contact time, with agitation.

Further laboratory tests indicated that 100 grams of paraformaldehyde dissolved completely in 300 ml. of water in 20 minutes, at 60° C., with agitation and when 0.1 percent NaOH on paraformaldehyde had been used.

At this point a test in the Woodland Factory was made. A solution of 100 pounds of paraformaldehyde was prepared by adding 3 ounces of caustic to 140 gallons of house hot water at 90° C., then adding the paraformaldehyde while stirring. Steam for heating was turned on for 1½ minutes and the resultant temperature of the mixture was 70° C. Depolymerization was complete in 23 minutes and the temperature then was 64° C. The caustic added had raised the house hot water to 10 pH.

For routine factory practice depolymerization and solution of paraformaldehyde has worked out as follows:

Equipment: A tank of about 200 gallons capacity (which should be covered and provided with a vent to the outdoors if located indoors); a

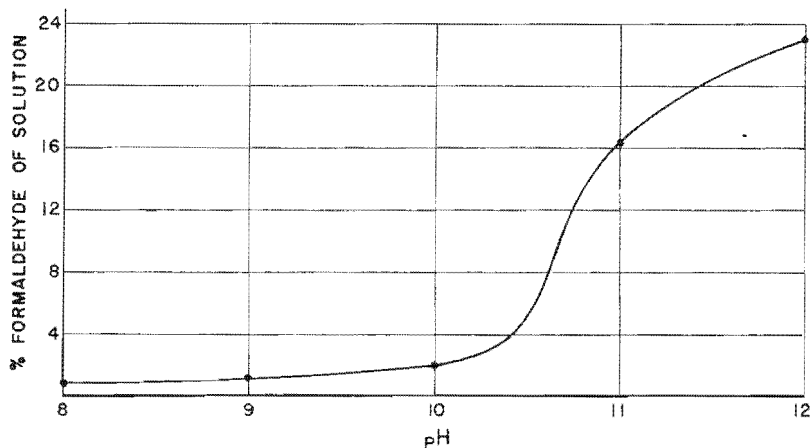


Figure 1.—Effect of water pH on depolymerization of paraformaldehyde. Percent formaldehyde by weight in solution, after 20 minutes at room temperature is plotted against pH of water.

water supply to tank; provision for heating by steam injection; provision for agitation such as a Lightnin' mixer; pump and lines to carry formaldehyde to desired points of application.

The diffuser operator prepares a new solution as the tank becomes empty. One hundred fifty pounds of paraformaldehyde are mixed with about 160 to 165 gallons of water, with sodium hydroxide added to bring the pH to 10.5. The mixture is heated by steam injection to 40° C., and agitated. Nearly complete dissolution is reached in about 30 minutes. The solution thus prepared will be approximately 10 percent formaldehyde.

By increasing the solution temperature or increasing the pH, the solution rate of paraformaldehyde may be increased. Similarly, the formaldehyde solution concentration may be increased. Figure 1 depicts a plot of pH versus paraformaldehyde solution.

Feasibility of depolymerization of paraformaldehyde has resulted in important savings in the cost of diffuser bacteria control.

References

- (1) The Merck Index. 1952. Sixth Edition, p. 719.
 - (2) Chemical Abstracts. 1945. 39:4083.
 - (3) U. S. Patent 2,460,592, by A. R. Miller, Jr., assigned to the Goodrich Rubber Co., February 1, 1949.
-