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Serendipity and Discovery

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Serendipity/*n* (fr. its possession by the heroes of the Per. fairy tale *The Three Princes of Serendip*): the gift of finding valuable or agreeable things not sought for. ("Webster's Seventh New Collegiate Dictionary")

The typical story of discovery in the industrial laboratory is one of search and find. However, there is the occasional happy discovery which is the result of serendipity. A case illustrating this is the story of how poly(ethylene oxide) became a valuable article of commerce.

The time was the summer of 1951, and the place was the South Charleston, West Virginia, laboratories of Union Carbide Corporation. A new plant to produce a reaction product of ethylene oxide was being designed. Reaction data were required and experiments were being run to satisfy these needs.

Ethylene oxide is a gas at normal laboratory temperatures. It boils at 10.4°C at atmospheric pressure. The most convenient way to store it is in metal cylinders which are equipped with valves for filling and use of the contents.

Two chemists, George Fowler and Walt Denison, were using ethylene oxide from such cylinders in their work. One of the cylinders obtained from the stockroom was found to be unusable. When the valve was opened, what came out was a black and viscous liquid instead of the clear, free-flowing liquid they expected. This cylinder was set aside and another found which behaved normally. The required reaction studies proceeded and design data were collected.

Fortunately, Fowler and Denison were curious about that "bad" cylinder of ethylene oxide. They retrieved it and examined its contents carefully. First, they found that when the black liquid was allowed to stand in the open at room temperature it turned into a black, horny, tough solid.

Then, they determined that the solid could be dissolved in water. When the water solution was filtered, a black powder remained on the filter paper. When the water was evaporated from the filtrate, a white, horny, tough solid remained. The white solid dissolved easily in water and even when dilute, the solutions were noticeably viscous.

Well, here was something interesting! A material that in low concentration altered the viscous properties of water might have some beneficial applications. George and Walt were pretty sure that it might be a polymer of ethylene oxide, but a unique one. The ethylene oxide polymers they had experience with were liquids or brittle waxy solids and had minimal effect on the viscous properties of water.

Analysis of the black precipitate on the filter paper showed that it contained iron. It was also magnetic. These clues generated an experiment. Some ethylene oxide was sealed in a glass tube with some magnetic iron oxide, Fe_3O_4, and kept in the dark at room temperature. At the end of five weeks, the contents of the tube resembled the solid from the "bad" ethylene oxide cylinder. In subsequent experiments, higher rates of polymerization were observed at elevated temperatures. In addition, Fe_2O_3 was found to be a catalyst, although not as effective as Fe_3O_4.

The contents of the "bad" cylinder were now explainable. Ethylene oxide had polymerized slowly in storage to a high molecular weight poly(ethylene oxide) as a result of being in contact with Fe_3O_4, possibly generated when the cylinder had been fabricated. In 1933, Staudinger and Lohman at the University of Freiburg had prepared varieties of poly(ethylene oxide) of varying molecular weight in slow polymerizations taking from two months to two years using strontium, calcium, or zinc oxides as catalysts. The products were described as hard and elastic, soluble in water. Their work was published in Justus Liebig's *Annalen der Chemie* where it lay unnoticed. Eighteen years later Fowler and Denison rediscovered essentially the same products in an environment where their potential value could be recognized. They then started a sequence of events necessary for successful commercialization of a new product.

They wrote reports on their work taking pains to see that the existence of the material and their observation about the effect on the viscous properties of water were made widely known to other chemists. Soon, requests for samples came. Polymer scientists wanted to measure bulk and solution properties. Applications chemists wanted to see how the water thickening properties of the new material could be put to practical use. The information on bulk and solution properties, which suggested new uses, was transmitted to the applications chemists. These fellows found that the products available were not exactly right for particular applications so requests for products of altered molecular weight went back to the discoverers.

It soon was apparent that the products needed could not be supplied with the original polymerization technology. A group of polymerization chemists was brought in to find the means to make a wider range of products. They found new catalysts and polymerization techniques to make products covering a wider range of molecular weights. A cycle of new polymer preparation, property measurement, and applications work continued for some time until a number of products were defined, tailored to a range of applications. Finally, process development chemists were given the task of finding a way to make the products on a commercial scale. A manufacturing unit was built and a new product family was launched. This story is rather typical of the way new polymer products find their way from the bench to the marketplace.

Today, there is a family of poly(ethylene oxides), called POLYOX® Water Soluble Resins, ranging in molecular weight from one hundred thousand to five million. Each member is used commercially for its unique place in the spectrum of properties.

Poly(ethylene oxide) is truly thermoplastic so it can be extruded or calendered into sheets of water-soluble film. Packaging specialists made use of the film to make water-soluble packages of measured quantities of materials. When thrown into an aqueous mixture, the package dissolves and the contents are released into the mixture. Packaging of household detergents, bleaches, and agricultural spray ingredients are some applications which have been made. Agriculturists made use of the film for precision planting of small-seed crops. Seeds are imbedded in strips of film at predetermined intervals. At planting, the "seed tape" is placed in a shallow furrow and covered with soil. On germination, plants emerge at precise intervals, spaced to simplify cultivation and harvesting.

Every third atom in poly(ethylene oxide) is oxygen. The unshared pairs of electrons enable formation of association complexes. As a result, it has good coagulating properties which are used to protect the environment. With it, finely divided clays, silicas, or coal fines are removed from the wastewater from mining operations before the water is returned to the streams and rivers.

The original observation of ability to increase the viscosity of water is used in a variety of ways. Small quantities in deicing fluids keep the fluid in contact with aircraft surfaces by retarding run-off. The same property is used in thickening water-based paints, paint removers, and metal lubricants.

Solutions in water feel silky to the hands. This property is used, in addition to thickening ability, in formulating cosmetics, lotions and shampoos, soap bars and liquid dishwashing detergents.

The higher molecular weight products are viscoelastic in water, giving solutions which are "stringy" and sticky. This property may be used in preparation of denture adhesives.

One of the most fascinating properties of poly(ethylene oxide) is that addition of trace quantities causes reduction in friction of water flowing through pipes and hoses. This has been applied in the building trades to enable pumping of concrete mix through hoses at construction sites. And in fire-fighting, smaller hoses can be used to deliver the same amount of water or streams can be projected at fires from greater distances or to greater heights with the pumps already installed in fire truck. The development of this application was a particularly trying one. It is no simple matter to add precisely controlled amounts of poly(ethylene oxide) to water going through a pumper under field conditions. The means of addition must foolproof; there is no time to fiddle with an unreliable feeding system when a fire is raging. The first field attempts were hair-raising. Metering devices failed and water lines became constricted with undissolved material. When lines were opened to remove the constrictions, water-poly-(ethylene oxide) mixtures poured out on the streets. As mentioned above, poly(ethylene oxide) solutions, especially concentrated ones, tend to be slippery. So these first trials often resembled silent movie comedies with firemen trying to keep their footing in the equivalent of a sea of banana peels. But perseverance paid off and the product is in use.

POLYOX® poly(ethylene oxide) possesses a very low degree of toxicity. The Food and Drug Administration recognizes its use in lotions, drug, and cosmetic products and even as a direct additive for stabilizing the "head" on beer.

In this story we see the importance of several things. Two chemists, who were pursuing other objectives, yielded to serendipity; how many might have thrown away "that lousy cylinder" of ethylene oxide? And they saw the importance of letting others know what they had done. They were not polymer scientists nor applications oriented. By letting the right people know what they had done, the necessary follow-ups ensued to realize commercialization.

Serendipity is somewhat synonymous with luck. Just suppose that the polymerization in the cylinder had been complete. There would have been no monomer to serve as solvent and the polymer would have remained in the cylinder unseen. Would Fowler and Denison have been curious enough to have cut the cylinder open to find out why nothing came out?

Note

Dr. Fowler, now retired, shared his experiences and made important contributions to the preparation of this article. His address is 309 Clayton Rd., Chapel Hill, NC 27514.