

The case of the barnacled crystal

G. T. KOHMAN
Physical
Chemistry

One day, Western Electric engineers inspecting the growth of EDT crystals at their Allentown plant made a startling observation. The crystals had started to grow what looked like barnacles (Figure 1) but which turned out on closer examination to be crystals of a kind never seen before. Worse—the mysterious intruder had caused the EDT crystals, urgently needed for the Bell System's coaxial program, to stop growing and appeared to be feeding on them.

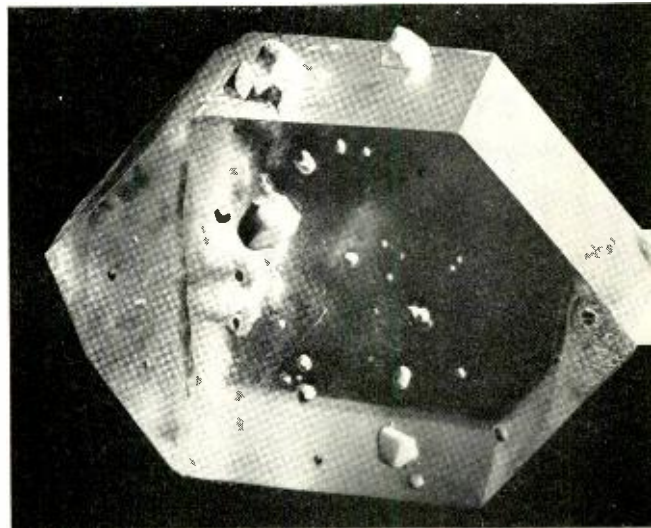
Alarmingly the infection spread from tank to tank, then over to the experimental tanks at the distant Murray Hill laboratory and even to the Western's production unit at Kearny where it appeared as a white fungus on crystal plates. Crystal production was threatened with complete shutdown and the situation was referred to the Laboratories where EDT crystals originated.

There the problem was attacked by a team of physicists, chemists and crystallographers in close cooperation with the Western Electric engineers. Within three days they had discovered the remedy and soon thereafter EDT production was headed back to normal. How this was done is a dramatic illustration not only of fundamental chemistry and physics in the role of Sherlock Holmes in the communication art, but also of the effectiveness of the team method of attack characteristic of the Bell Telephone System.

EDT (short for "ethylene diamine tartrate") is a piezoelectric synthetic crystal developed by the Laboratories for use as a substitute for scarce quartz in the filters of telephone carrier systems. Each crystal is grown^{*} from a "seed," a section of EDT crystal, in a super-saturated solution of ethylene diamine tartrate. As the seeds rotate in the solution, molecules of EDT

pass out of solution to precipitate on the seed in rigid crystallographic order and in a few weeks the seeds grow large enough for the cutting of plates for filters.

It had been known from the start that "veils" and other flaws mar the crystals if the strictest control is not exercised over the concentration and temperature of the growing solution. But this was a new phenomenon in which the solution was apparently



sprouting new crystals of unknown origin. This the solid state group quickly established by measurements of crystallographic angles and by X-ray diffraction studies. Meanwhile, the physical mechanics group showed that the new crystal was worthless as a filter element because of its very slight piezoelectric activity.

That the new crystal was not due to any radical changes in the growing solution was obvious when the solid state group showed (1) that the new crystal grew well from freshly prepared solutions, (2) that the EDT crystal could grow well from the old solution, and (3) also that it grew well from

^{*}RECORD, October, 1947, page 357.

a solution of the new crystal alone, in the absence of any seeds of the new crystal. Furthermore, the organic chemists were able to recover from the new crystals the exact ingredients from which the growing solutions were initially prepared!

The analytical chemists found that the composition of the strange crystal was the same as that of EDT except that it contained exactly one molecule of water for each EDT molecule thus establishing it to be a monohydrate of EDT. The solid state group also showed that when this water molecule was removed the intruding crystal broke down into a mass of very small EDT crystals.

These findings established that the solution itself was not to blame; so at any rate growing solutions need not be discarded. But what was the explanation?

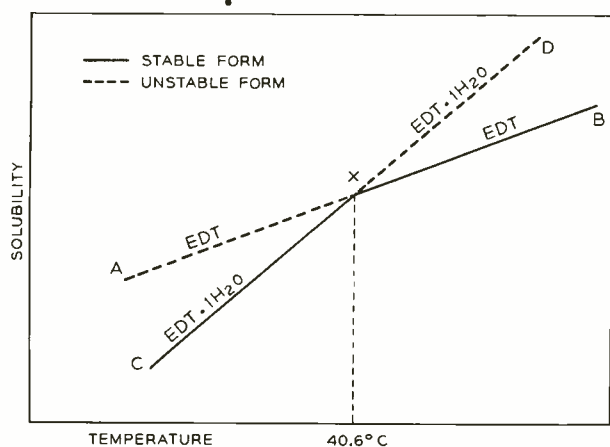


Fig. 1—EDT solubility relationships.

Physical chemists possess in the phase diagram or solubility relationship a powerful tool for determining under what conditions one or the other of several crystalline forms of a compound can be grown from solution. A few solubility determinations by physical chemists were sufficient to establish approximately this relationship as shown schematically in Figure 1. From this it is obvious that at temperatures below approximately 40 degrees C. the hydrate is the less soluble form. It also follows from physical-chemical principles that the less soluble form is the stable form in the presence of a saturated

solution and theoretically the two forms of EDT crystal can exist in equilibrium with the solution only at the point of intersection X of the two curves of Figure 1. The relationship shown in Figure 1 requires that at any point within the area AXC, the EDT crystal must go into solution and recrystallize as the hydrate if a hydrate seed crystal is present. At any point in the area DXB the situation is reversed and only the EDT crystal can grow.

Now the crystal plant had been operating at a growing temperature of 38 degrees C, in the region favorable to the formation of the hydrate if by chance a dust or other foreign particle of the right structure for a seed is carried into the tanks. Fortunately the point of intersection of the two solubility curves shown in Figure 1 occurs at only three degrees above the temperature at which the plant had been operated and it was a simple matter to raise the growing temperature by 4 degrees C to above the danger point.

To harassed engineers, under pressure to produce EDT crystals because of the critical quartz supply situation, this slight increase in temperature hardly seemed adequate to salvage a process which the mysterious intruder had sabotaged. Yet surely enough, in conformance with the solubility relationship shown in Figure 1, when the temperature in the Allentown tanks was raised by 4 degrees C, the hydrate began slowly but definitely to shrink while the EDT crystals recovered their normal rate of growth.

There remained the serious difficulty of preventing the formation of the hydrate in the processing of crystal plates for filters. In the Kearny plant, where it had been the practice to cut EDT crystals by techniques involving the use of water, the hydrate was found to sprout like a fungus growth on the carefully cut plates and the powdery hydrate seriously interfered with the extremely fine adjustment of the crystal plates to the desired frequency. These difficulties were gradually resolved by protecting the crystal from moisture as far as possible and by processing the crystal when possible above 40 degrees C.

In the Laboratories, where previously

THE AUTHOR: G. T. KOHMAN received the B.S. degree in 1920 from the University of Kansas, and then attended Yale University for graduate study. In 1923 he received the Ph.D. degree and joined the Laboratories. For some years he was in charge of investigations of the absorption of water and oxygen by organic substances and of the physical and chemical behavior of the paper and impregnants used in condensers. More recently he has been responsible for groups working in the chemistry of ceramics, crystal growth, and contact phenomena, and of dielectric measurement.



EDT crystals had been grown in large numbers by a "dropping temperature" process, the appearance of the hydrate rendered this process inoperative because as soon as the temperature of the growing solutions reached 40 degrees C the hydrate appeared in the solutions, causing the EDT crystal to stop growing and in some cases actually to redissolve.

The hydrate contains all the ingredients required for the growth of EDT crystals and it was found that it can be recovered from solution in a much purer form than the EDT salt which, until then, had been used to prepare the growing solutions and to keep them up to strength. At temperatures above 40 degrees C hydrate added to the growing solution dissolves completely in the solution in which EDT crystals are growing and cannot reform as the hydrate. Besides it is safer to feed to the growing solution, as crystal fragments which may

accidentally be carried into the growing tanks do not act as EDT seeds causing spurious growth. Growing solutions prepared and fed with the hydrate may be used much longer before the need for reprocessing to remove impurities and, because the hydrate crystallizes from contaminated solution in pure form, it is now used to advantage in the recovery of salt from spent growing solutions.

Had it not been for the alertness of the Western Electric engineers in detecting the presence of a new crystal in their growing tanks the production of EDT crystals could have been seriously delayed. The effectiveness of an organization where the services of a number of specialists in a variety of fields can be promptly brought to bear on an emergency problem, has been impressed on the writer who, after one look at the new crystal, had visions of a prolonged shutdown of the crystal plant.

Thermistor Aids in Measuring Humidity

Application of the Thermistor to measurement of atmospheric humidity is described in a recent article by Kenneth H. Jehn. The method is to mount a D-177232 Bead Thermistor on a mechanism which alternately dips it in a reservoir of water lifted up into the air stream to be measured. The usual difficulty of clogging of the wick is thus avoided. The wet bulb temperature of the air is measured by an electrical circuit including the Thermistor. Quick responses in changes to temperature of the Thermistor give the apparatus a lag of about 3 seconds which is approximately one-tenth of the lag of the usual mercurial psychrometer.*

* "Wet Bulb Temperatures without a Wick"—*Review of Scientific Instruments*, September, 1949.