Crystallization of Sucrose with Sonic Waves[1]

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The graining of sucrose syrups by sonic waves has already been reported in a preliminary way. (8) (9) (10) (11) (12)[4] This report continues these studies and considers the mechanism of the action in some detail.

Previous Work

There is a voluminous literature on the generation, properties, and effects of sonic and ultrasonic waves, (2) and some of it deals with crystallization processes. (4) Unfortunately, little of this latter small group is concerned specifically with sugar crystallization. A German patent (1) in which vibratory treatments are claimed to improve sugar boiling is one of the two publications which, to the writer's knowledge, has appeared since the last report from this laboratory. The other is a note (5) in which the author reports that he was unable to nucleate honey by prolonged irradiation. It is apparent from the data listed that considerable alteration of the syrups occurred during the treatment.

Method

A wide variety of sonic and ultrasonic equipment is available. The magneto-strictive type was used in most of the present investigations and the essential characeristics of this equipment are represented in Figure 1. The outstanding feature of this apparatus is the exceptional high power levels delivered by the transducers. These intensities, at their maxima, were estimated to be 4 and 14 sonic watts/cm.^{2} at 8 kc. and 1.1 mc., respectively.

Mechanism

It had been assumed in our earlier work (9) that a homogeneous mechanism is entailed in the formation of crystal nuclei by ultrasonic irradiation. However, careful observations on sugar solutions are not in accord with this hypothesis. The most convincing type of experiment indicating this situation is one in which the irradiation is performed under virtually sterile and isolated conditions. In this case, the otherwise usual positive effect is greatly reduced, and even absent in some cases. This suggestion of a heterogeneous mechanism is in accord with the

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[1] This work was done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract was supervised by the Western Utilization Research Branch of Agricultural Research Service, Albany, California.

[2] Much of the work summarized in this paper is taken from the M.S. theses of Messrs. Bujake and Casazza.

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[4] Numbers in parentheses refer to literature cited.

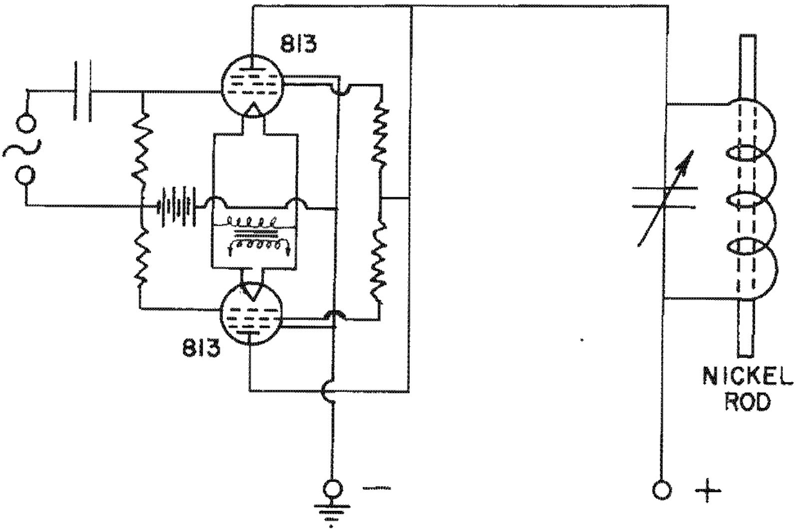

Figure 1.—The electronic circuit consisted essentially of a standard oscillator with sufficient grid driving power for one or two stages of power amplification. The above circuit, for example, is typical of the final stage used to drive magnetostrictive transducers.

For barium titanate transducers less power was usually required, a single stage being ample for the smaller transducers. These were inductively coupled to the final tank circuit.

calculation that the energy equivalent of even megacycle radiation is only calories per mole, whereas that required for homogeneous nucleation is of the order of kilocalories.

Under ordinary operating circumstances, truly homogeneous conditions do not prevail so that irradiation produces an apparent acceleration of the adjustment of supersaturated sugar solutions, just as in many other systems. This overall effect is the net result of simultaneous and consecutive nucleation and growth. Since nucleation without growth is impossible in a supersaturated environment, the separate contributions of these two steps must be resolved under conditions of growth without nucleation. This is accomplished by attaching a single crystal directly to the transducer bar. With this arrangement, it is observed that growth under irradiation proceeds only slightly faster than normal. Figure 2 displays the complete log of such a run. The slight increase (25 percent) under irradiation is more than reproduced (45 percent) by rotating the crystal at 200 r.p.m. without irradiation. Similar results are obtained at other concentrations and other frequencies: so that we may conclude that irradiation does not accelerate the absolute growth rate more than stirring at

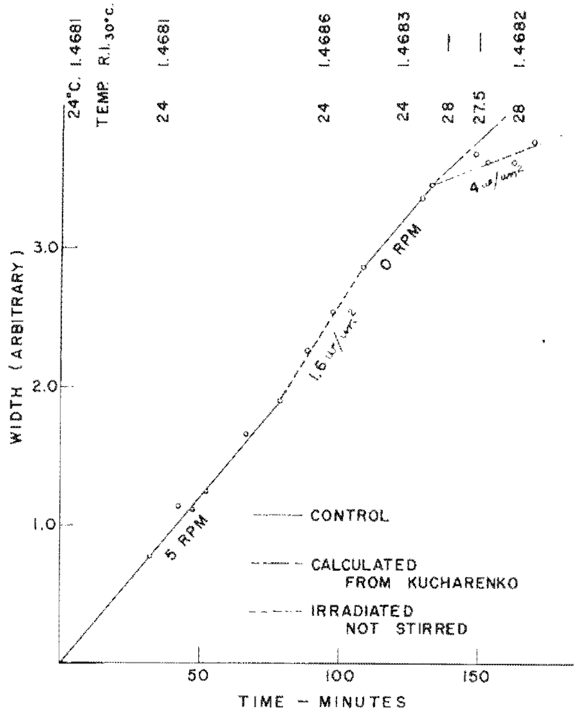

Figure 2.—Growth rate under irradiation at 8 kc.

200 r.p.m. The principal effect of irradiation is then on the nucleation process, and the following effects have been observed with solutions prepared in the usual manner.

Variables

Power. It is observed at effective frequencies that graining is produced only if exceedingly high power intensities are impressed. This more or less critical energy level is about 2 sonic watts/cm.^{2} at 8.8 kc., and corresponds with the onset of cavitation. Excess energy above this level is relatively ineffective. Figure 3 illustrates this pattern for several conditions. Similar results are realized at other frequencies and other temperatures, and the threshold power requirement remains between 1 and 2 sonic watts/cm.^{2} in all cases. Qualitative experiments indicate that the minimum power level is elevated by increased viscosity, but in the case of stronger solutions the enhanced effect of higher supersaturations is greater than the reduction occasioned by the increased viscosity.

Frequency. The 10^3 to 10^5 c.p.s. band of frequencies is found to be effective, provided the critical power level is exceeded.

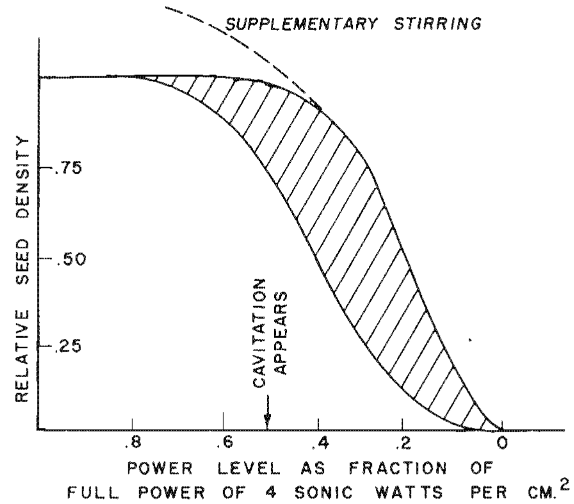

Figure 3.—Critical power level.

Within this spread there is a slight optimum at the 10^4 range. While most of the process variables reported here were observed at a frequency of 8.8 kc., they have been confirmed in a larger unit at essentially 28 kc. This latter frequency is above the audible range and is preferred for continued work.

Concentration. With all other conditions the same, the seed density developed by irradiation increases with respect to controls, as the supersaturation is increased. For instance, a typical series in which only the supersaturation was varied, follows:

Oversaturation	1.1	1.2	1.4	1.5	1.75	2.0	2.2
Relative seed density with respect to control	1.0	2.0	3.5	3.0	5.5	7.0	12

The reproducibility of such a series is not good since the footings generated depends upon the initial occurrence of foreign or potential nuclei. However, in similar experiments with seeded syrups, or with single crystal footings, the same increase in final seed density is observed as the concentration is increased.

Duration of Irradiation. Continued irradiation increases the crystal population in an autocatalytic manner. However, the uniformity of the final product suffers considerably as irradiation proceeds, since both nucleation and growth continue simultaneously during this period.

Nuclei Density. If one irradiates a strong syrup with the bar transducer, cavitation loci appear at definite points according to the size, shape, and arrangement of the system. The crystal nuclei are generated, presumably within these small volumes. They may then be dispersed and grown to visible size in order to estimate the number created by the treatment. In this way, a density of approximately 10^8 per ml. of cavitation space was observed after irradiating a 20 percent oversaturated syrup at 30° C. for 10 minutes.

In another similar experiment in which the nuclei were dispersed as generated, a total of 1.5 x 10^6 centers was established throughout the entire space of 10 ml., or 1.5 x 10^7 per unit of originating volume. (These estimates of 10^7 to 10^8 nuclei/ml. may be compared to a typical graining procedure of about 10^5 particles/ml. of fondant in low grade work (3). The refractometric growth curve of this dispersion was then compared to those of known composition and found to be equivalent to a 1/30,000 slurry of 2 μ diameter seeds, 1/1,700 of 50 μ, or 1/330 of 160 μ particles. All four of these mixtures then contain approximately the same growing area of crystal footings. Since the area of a crystal is proportional to the square of its diameter, we may estimate that the size of the particles generated during the 10 minute irradiation is between 3 and 4 μ (4.0, 3.4, and 4.2 μ. respectively).[5] Since the linear growth during this period would have amounted to almost 20 μ, we may surmise that the sonic field has promoted a tremendous amount of false grain.

Temperature. No unusual effects of temperature are observed over the 30-70° C. range.

Natural Syrups. The above process variables were examined in detail with two beet syrups at standard thick juice and low machine grades, and no deviations from the white syrup patterns were observed. Similar tests on a low purity cane product yielded essentially the same results.

Uniformity. The stimulation of grain formation by sonic irradiation has led to the suggestion (10) that improved uniformity may result from such treatment. However, marked beneficiation in this respect results only after short periods of irradiation. During any extended exposure the dispersion of sizes continues to widen because of the simultaneous autocatalytic generation and growth processes. To minimize these divergent effects the treatment times must be extremely short, and to realize sufficient grain density the transducer area must be in-

[5] These calculations have been refined to account for the distribution of sizes and accretion during the exposure time. The analysis does not reduce the above estimate by more than an order of magnitude. It is suggestive to point out that this size (10^4 to 10^5 cm.) is within the domain of the mosaic theory of the structure of solids, but well above that (10^6 to 10^7 cm.) of the critical nucleus required for homogeneous nucleation.)

creased to multiply the seed density to the population required for the finished strike.

None the less, even with this limitation it has been possible, in experimental strikes with the bar transducer, to realize uniformities of 20 percent or less, as expressed by the coefficient of variation (2). It appears likely that this figure may be improved in a new pilot plant unit which has been constructed recently.

Summary and Conclusions

The mechanism of sound activity is heterogeneous, and not homogeneous.

Treatment with sonic waves accelerates the adjustment of supersaturated sucrose solutions, both pure and impure. This treatment has no special effect on the rate of growth of single sugar crystals, so that the observed overall increase is due almost entirely to enhanced nucleation by false grain formation.

The effects of sonic graining become more pronounced with increasing supersaturation and time of irradiation. A threshold power level of about 2 sonic watts/cm.[2] is necessary to obtain any significant results, and excess energy above this level is relatively ineffective. The optimum frequency is in the neighborhood of 10 Kcs. No unusual effects have been observed over the temperature range 30-70° C.

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