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▲ To whom inquiries should be directed.

Influence of Power on Quality of Emulsions Prepared by Ultrasound

DONALD M. HIGGINS* and DONALD M. SKAUEN▲

Abstract □ The effect of ultrasonic power on a mineral oil-surfactant-water emulsion system was demonstrated. An optimum amount of energy was required to produce the best emulsion. Exceeding the optimum requirements produced coalescence phenomena. The best emulsions resulted with optimal surfactant concentrations, at optimal HLB values, and at highest power levels. In the emulsions studied, the HLB and surfactant parameters were more important than the power parameters.

Keyphrases □ Emulsions, mineral oil-surfactant-water—effect of ultrasound, HLB, surfactant, and power parameters □ Ultrasound—effect on mineral oil-surfactant-water emulsions, HLB, surfactant, and power parameters

In recent years, many workers have utilized various types of ultrasonic generators to form emulsions. Beal and Skauen (1) investigated the effect of exposure time and sample geometry on the quality of the emulsion system. Haavisto and Hagner (2) studied the efficiency of emulsification with ultrasound with and without emulsifiers. Myers and Goodman (3), Singiser and Beal (4), Marshall (5), and McCarthy (6) all described experiments using a liquid whistle generator. In these studies, the main parameters considered were the emulsion systems themselves and the length of insonation. Kann and Tester (7) utilized a step-horn transducer with fixed frequency and variable power. However, they concerned themselves with the emulsion rather than instrument parameters.

Since little attention has been focused upon the effect of power on the quality of emulsions manufactured by step-horn ultrasonic generators, this study was designed to determine what effects changes in ultrasonic power might have upon an emulsion system.

EXPERIMENTAL

Sonifier—The ultrasonic instrument[1] used in this study utilizes a power supply, a sonic converter, and a step-horn transducer. It

[1] Branson Sonifier model J-17V, Branson Sonic Power Co., Danbury, Conn.

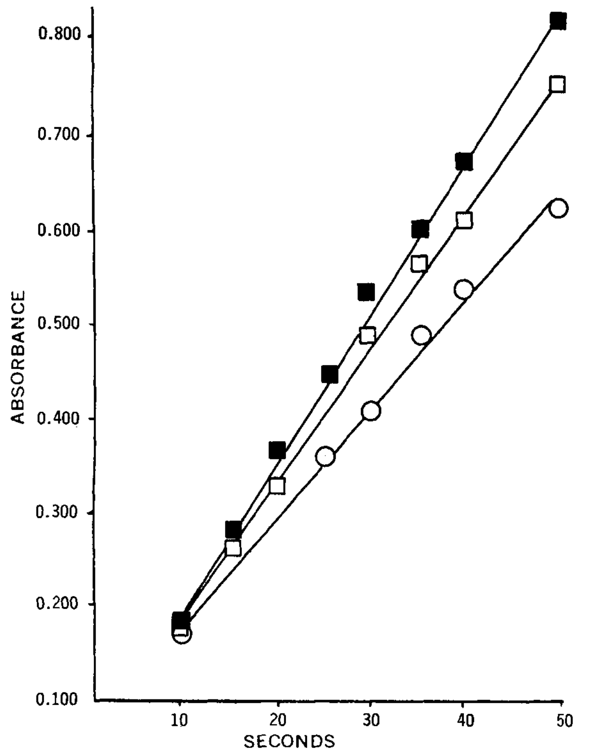

Figure 1—*Determination of Sonifier power levels using the colorimetric chlorine release method. Key:* ■, *power level 80;* □, *power level 65; and* ○, *power level 55.*

operates at a frequency of 20 kc. with a normal power output of 1700 in. lb./sec. The power supply is equipped with an activity level control with a dial marked off, in this instance, in arbitrary units from zero through 80. To use these units to estimate activity in the treatment vessel, a calibration must be performed. Once this is accomplished, the effect of a change in power setting on emulsification becomes more meaningful.

Cavitation—Among the several forces which occur during the process of emulsification with ultrasound that of cavitation is most pronounced (8, 9). Cavitation was defined by El'piner (10) as: "the formation of cavities by the liquid and their subsequent collapse, which is accompanied by intense hydraulic shocks. A cavitation bubble is formed by a temporary reduction of pressure in a particular volume inside the liquid if the pressure falls below the threshold of the strength of the liquid." One of the methods used to estimate energy delivered to the treatment vessel is a modification of that described by Weissler (11). This depends upon the liberation of

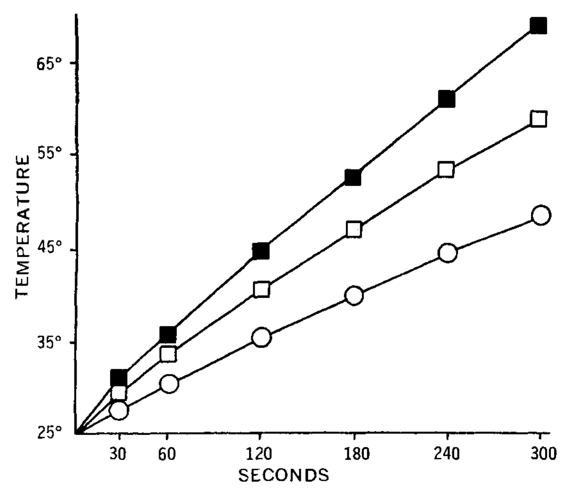

Figure 2—*Determination of Sonifier power levels calorimetrically. Key:* ■, *power level 80;* □, *power level 65; and* ○, *power level 55.*

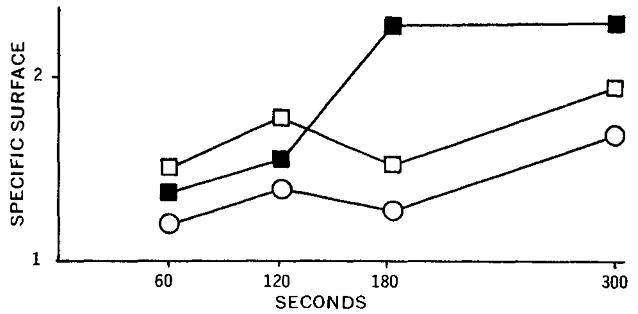

Figure 3—*Specific surface values of mineral oil-in-water emulsions prepared at various ultrasonic power levels at surfactant concentrations of 0.5% and an HLB of 10. Key:* ■, *power level 80;* □, *power level 65; and* ○, *power level 55.*

chlorine from a saturated solution of carbon tetrachloride in water when subjected to sufficient amounts of radiation to cause cavitation. The chlorine subsequently reacts with a dye, *o*-tolidine, to form a yellow-colored complex which is measured colorimetrically. This technique was used in this study.

With a colorimeter[2], a peak color intensity was observed at 435 nm. The color was stable for 12 min. The Beer–Lambert law was verified by developing the colored solution by irradiation with the step-horn for 70 sec. and assigning this the arbitrary concentration value of 100%. Various dilutions of this "full strength" color solution were made and absorbances were taken, and these were plotted against concentration. A straight-line plot passing through the origin resulted.

Since positioning of the step-horn relative to the sample is a factor in cavitation (12), the depth of immersion yielding the greatest amount of cavitation was determined by exposing test solutions of carbon tetrachloride and *o*-tolidine to insonation at different depths of immersion of the horn; the highest absorbance was obtained when the step-horn was immersed 1.27 cm. (0.5 in.). In all future experiments, this immersion depth was maintained.

The relative amounts of cavitation produced at activity dial settings of 55, 65, and 80 at exposure times of 10, 15, 25, 30, 35, and 40 sec. were determined. Results are shown in Fig. 1.

It was decided later to insonate the various emulsions for as long as 300 sec., making it necessary to validate the curves in Fig. 1 for as long as 300 sec. Because the absorbances dropped appreciably after 180 sec. of insonation, it was necessary to utilize another calibration technique. The following simple calorimetric method was adopted. One hundred-milliliter samples of water at 25° were insonated at the three power settings for 30, 60, 120, 180, 240, and 300 sec. and the increase in temperature of the water at each interval was recorded. Results are noted in Fig. 2. This method includes within it a number of sources of energy including cavitation. It is satisfactory, however, for the purpose of repetitive calibration of the instrument and for demonstrating that there are differences among the various power settings.

Preparation of Emulsions—The emulsions were 30% (w/w) light mineral oil[3] in water. The total weight of the emulsions prepared ultrasonically was kept to 100 g., an amount convenient to emulsify with the Sonifier. The emulsifying agents were blends of sorbitan monostearate[4] and polysorbate 60[5].

The emulsion ingredients were weighed directly in the container [a 120-ml. (4-oz.), amber, polyethylene bottle] in which the emulsion was to be made in the following order: water, oil, sorbitan monostearate, and polysorbate 60. Each emulsion was inverted 20 times just prior to being emulsified in order to premix slightly. The power supply of the Sonifier was adjusted to the desired level, and the step-horn was immersed in the emulsion to a depth of 1.27 cm. (0.5 in.). In most instances, it was necessary to use an ice bath to maintain a constant temperature (25 ± 2°). After the desired time of irradiation elapsed, the power was shut off. Aliquots of each emulsion were then removed and examined by a photomicrographic and counting technique similar to that described by Singiser (13).

[2] Beckman Spectronic 20.
[3] Drakeol No. 9, Penn Refining Co., Butler, Pa.
[4] Arlacel 60, Atlas Chemical Ind., Wilmington, Del.
[5] Tween 60, Atlas Chemical Ind., Wilmington, Del.

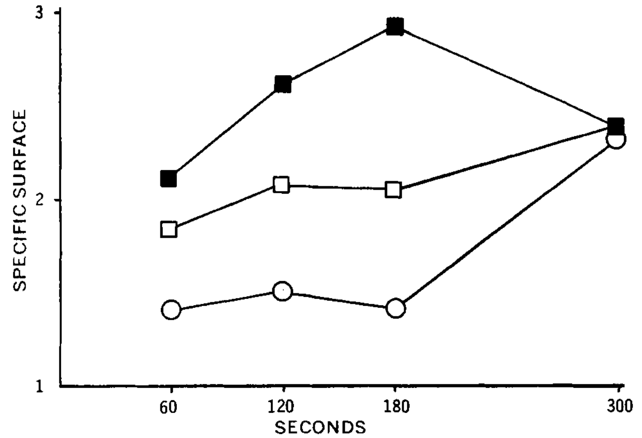

Figure 4—*Specific surface values of mineral oil-in-water emulsions prepared at various ultrasonic power levels at surfactant concentrations of 1.0% and an HLB of 10. Key:* ■, *power level 80;* □, *power level 65; and* ○, *power level 55.*

RESULTS AND DISCUSSION

In this study, emulsions were made at three different power levels, with four distinct times of exposure to ultrasonic waves and with three concentrations of surfactant blend: 0.5, 1, and 1.5% by weight. This was repeated using three different HLB values, 11.3, 10.0, and 9.0. The emulsions were evaluated on the basis of their specific surfaces (S_v) expressed in area per unit volume. The particles were divided into categories ranging from 1–2, 2–3, 4–5 μ, and so on up to and including 10–11 μ. All visible particles below 1 μ were included in the 1–2-μ category. Those above 11 μ were included in the 10–11-μ group. A total of 1000 droplets was counted by the photomicrographic technique for each emulsion studied, and the data collected were subjected to a size-frequency analysis.

Specific surface data were determined by the method suggested by Singiser (13). The midpoint of the class interval was taken as the diameter representative of each class. The best emulsion would be, by definition, one in which all of the particles counted were in the 1–2-μ interval. This emulsion would have a specific surface of 4.00. The worst emulsion would be one where all of the particles counted were in the 10–11-μ class interval and the specific surface would be 0.57. An emulsion midway between these two extremes would be one in which the 1000 particles were divided equally among all 10 class intervals. This emulsion would have a specific surface of 0.729.

At all three power levels, the absorbance values decreased after 180 sec. of insonation during instrument calibration with the carbon tetrachloride release method. Several explanations for this phenomenon including oxygen depletion, hydrochloric acid production,

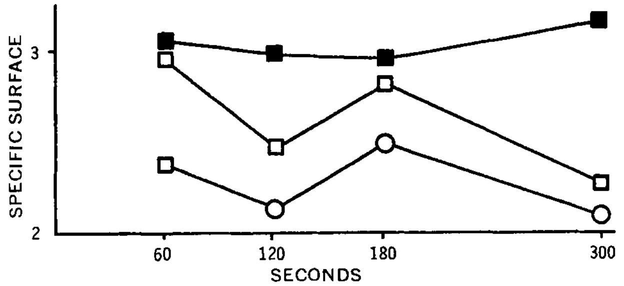

Figure 6—*Specific surface values of mineral oil-in-water emulsions prepared with various HLB values at surfactant concentrations of 1.5% and a power level of 80. Key:* ■, *HLB 11.3;* □, *HLB 10; and* ○, *HLB 9.*

and complex destruction may be offered. This effect will be investigated further.

Figures 3–7 illustrate in a general way the overall results of all of the emulsions studied. The emulsions in Figs. 3–5 were all prepared at an HLB of 10 and at 0.5, 1, and 1.5% surfactant, respectively. As shown in Fig. 3, at the two lower power levels of 55 and 65, there was very little change in specific surface; at the high power level of 80, a maximum specific surface seems to have been reached after 180 sec. Since energy input has a time function, it is possible that an extension of time of insonation for the 55 and 65 power levels might show a corresponding increase in specific surface.

As surfactant concentration was increased (Fig. 4), the specific surface values increased at power levels 55 and 65. In both Figs. 3 and 4, the influence of ultrasonic energy is easily observed. At the highest power level of 80 in Fig. 4, a linear increase in specific surface is seen up to 180 sec. followed by a decrease to 300 sec. This latter phenomenon possibly illustrates one important effect of ultrasonic energy, namely coalescence. With increased power, coagulation effects can become operative and would account for a decrease in specific surface. Since the possibility of destruction of the surfactant exists, solutions of both sorbitan monostearate and polysorbate 60 were subjected to insonation for 300 min. at maximum power. A modification of the method of Duncombe (14) was used to indicate the presence of free fatty acid as evidence of degradation of the irradiated solutions. No destruction occurred.

It is possible that Fig. 5 illustrates the effect of surfactant concentration as much as it does the effect of ultrasonic energy. The specific surface values were higher at the lower power levels, probably indicating greater availability of emulsifier at the initial stages. The very high value for the 80 power level after 60 sec. insonation tends to support this conclusion. The gradual decline in specific surface at 300 sec. may show coalescence effects. The lower power emulsions at 300 sec. evidently did not reach the threshold for this effect.

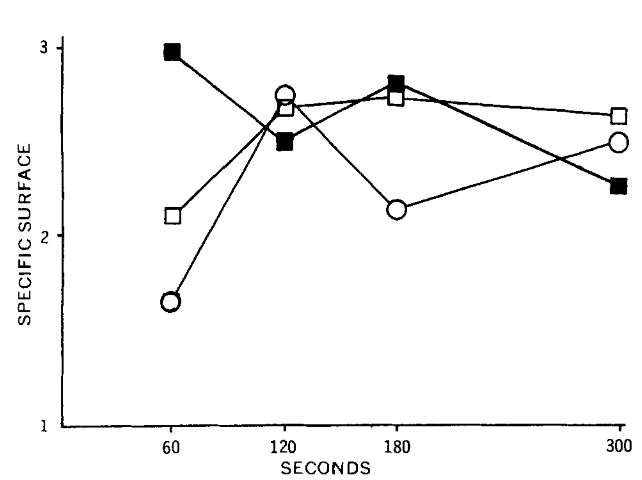

Figure 5—*Specific surface values of mineral oil-in-water emulsions prepared at various ultrasonic power levels at surfactant concentrations of 1.5% and an HLB of 10. Key:* ■, *power level 80;* □, *power level 65; and* ○, *power level 55.*

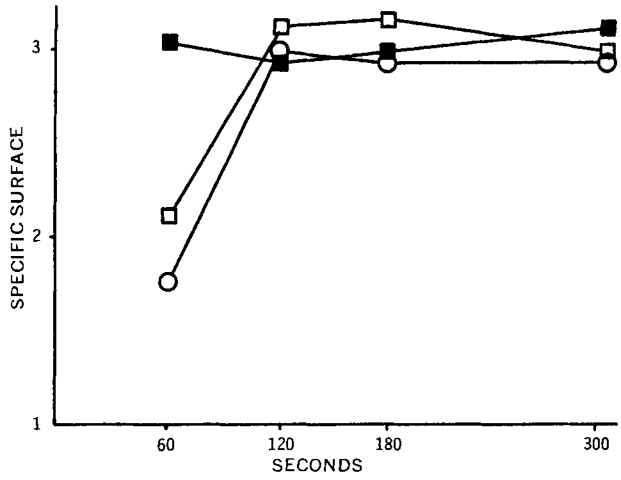

Figure 7—*Specific surface values of mineral oil-in-water emulsions at various power levels and optimal surfactant (1.5%) and HLB (11.3) levels. Key:* ■, *power level 80;* □, *power level 65; and* ○, *power level 55.*

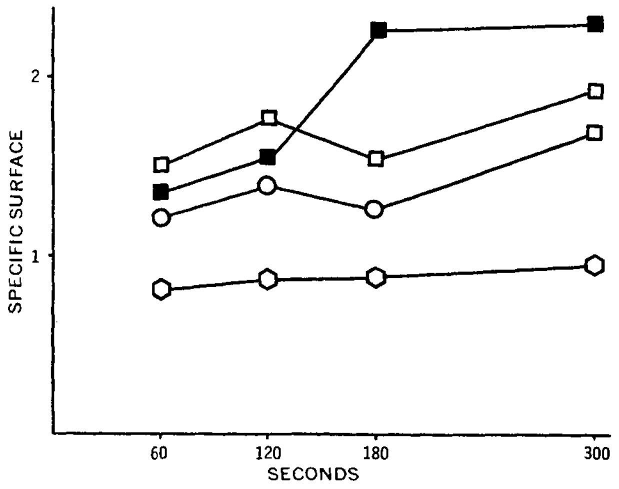

Figure 8—*Comparison of specific surface values of mineral oil-in-water emulsions prepared ultrasonically and with a Homomixer at surfactant concentrations of 0.5% and an HLB of 10. Key:* ■, *power level 80;* □, *power level 65;* ○, *power level 55; and* ○, *Homomixer.*

In general, all emulsions at all HLB and surfactant concentrations were better at high power levels than at the lower levels until coalescence effects became apparent. In most instances, a concentration of 1.5% surfactant produced better emulsions at all power levels.

The effect of varying HLB at the optimum concentration of surfactant (1.5%) and the highest power (80) is shown in Fig. 6. Predictably, the best emulsions are produced at optimal HLB conditions.

It is equally interesting to note (Fig. 7) that for those emulsions prepared with optimal HLB (11.3) and surfactant (1.5%) concentrations, the effect of power is less significant than the other two parameters after 120 sec. exposure.

As an aid in identifying the quality of the emulsions prepared, an Eppenback Homomixer was used to form the same emulsions. The comparisons are seen in Fig. 8. It appears that 300 sec. of exposure in the Homomixer does not improve the emulsion significantly. The specific surfaces of the Homomixer emulsions are lower than those of all Sonifier emulsions.

SUMMARY

1. When using the Sonifier, there is an optimum amount of energy needed to increase specific surface. If this level is not reached, maximum specific surface cannot be produced. If this optimum is exceeded, the maximum specific surface may not be obtained.
2. In general, for short insonation periods (180 sec.), the highest power settings produce higher specific surfaces than lower power settings.
3. The Sonifier produces oil-in-water emulsions with a very small particle size, which are superior to those prepared by the Eppenback Homomixer for the system studied.
4. The best emulsions were those prepared at optimal surfactant levels (1.5%), optimal HLB (11.3), and highest power (80).
5. The effects of HLB and surfactant parameters appear to be more important than the power parameter in the emulsions studied.

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* Present address: Pharmaceutical Process Improvement Department, Lederle Laboratories, Pearl River, N. Y.

▲ To whom inquiries should be directed.