Macrosonics in industry

4. Chemical processing

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Acoustic irradiation can result in increased inter-phase mass and heat transfer rates. The second-order acoustic effects of cavitation, interfacial instability, radiation pressure and acoustic streaming are responsible for the enhancement in these rate processes. The application of sonic and ultrasonic energy in industrial processing is reviewed. A number of units using acoustic energy to enhance rates of conventional unit processes, for example, drying, solid-liquid extraction, etc, are described. In addition, new applications in waste water treatment and oil-water emulsion fuels are described. The development of newer, more efficient generators should lead to a greater use of acoustic energy for large-scale industrial processing.

Introduction

The growing importance of industrial macrosonics is evidenced from the number of review papers.[1–4] The application of sonic and ultrasonic energy in the chemical processing industry can be classified into two categories: (a) applications in which acoustic methods yield a product superior to that obtained by conventional means (eg, an emulsion with smaller and more uniform particle size distribution) and (b) applications where acoustic energy is used to enhance the rates of conventional unit operations (eg, solid-liquid extractions).

A vast amount of exploratory research has been carried out in the laboratory to study the effects of acoustic energy on different processes. While the feasibility of using acoustic energy has been demonstrated in a number of applications, the 'scale-up' from laboratory experiments to pilot plant operation and then to large-scale industrial units has been slow in developing. With the advent of newer, higher intensity generators it should be possible to make the transitions from batch studies to continuous processing units more easily.

The mechanisms producing the observed increased rates in transport and unit operations processes can be divided into two categories: *first-order effects* (fluid particle displacement, velocity, and acceleration) and *second-order effects* (radiation pressure, cavitation, acoustic streaming, and interfacial instabilities). The radiation pressure is a secondary pressure which can bring about levitation of certain objects. Cavitation can result when high-intensity acoustic waves are passed through liquids producing small bubbles in the liquid. On collapse, the contents of the bubbles are compressed to very high temperatures and are capable of producing shock waves. In addition to cavitation and the oscillatory particle motion produced by the acoustic waves, one can also induce secondary flows commonly known as acoustic streaming. At fluid-fluid phase boundaries one is also able to induce interfacial instabilities as a result of the to-and-fro motion of the fluid particles. The phenomena of cavitation, acoustic streaming, and surface instabilities have produced increased rates of heat and mass transfer, chemical reactions, defoaming, and emulsification in a wide variety of chemical and physical systems. Usually, it is one or more of the second-order effects which are responsible for the enhancements in the transport process.

In the review that follows we shall deal with the current applications of sonic and ultrasonic energy in chemical processing. We shall also outline potential areas which hold promise of commercial exploitation.

Food industry

The food and beverage industry has the potential of utilizing sonic energy for treating heat sensitive materials without loss of flavour, taste or other damage.

Beverages

An improvement in colour, cloud, viscosity and yield of orange juice by ultrasonic treatment is claimed in a recent Spanish patent.[5] A process for the extraction of apple juice by the treatment of a fine apple pulp with ultrasonic energy of frequency 20–300 kHz and intensity 2.8 W cm^{-2} is described by Coltart and Paton.[6] In wine manufacture, the 800 kHz ultrasonic treatment of grape 'must' for 5–10 minutes before fermentation is claimed to increase the quantity of esters (ethyl lactate and ethyl caproate), isobutanol, isopentanol, optically active pentanol and hexanol in the wines and also improve their flavour.[7] In addition, the use of ultrasonics to clarify wines by precipitating potassium bi-tartrate without any deleterious effect on the chemical composition of the wines is reported.[8] Here an ultrasonic treatment of 1.5–2 hours (compared with 4–10 days for the conventional process) is required for complete precipitation and the resulting wine is stable for one year. The

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authors claim the ultrasonic settling process can be readily used.

The use of ultrasonics in the dairy industry is outlined by Mann [9] and Tobler.[10]

Food

Tudorie and Alexandru [11] describe a process for the decolouration of soybean oil using active earths with ultrasonics at 800 kHz, 80°C and 10–30 minutes irradiation time. Savings in the amount of earth used and the time needed are claimed. A review of the use of ultrasonics in the food industry is given by Saroun.[12]

Solid-liquid extractions

In the area of inter-phase mass transfer, solid-liquid extraction appears to be most greatly enhanced by the application of ultrasonic waves. Studies in our laboratory on the ultrasonic extraction of sugar from sugar beets show that while acoustic streaming enhances the extraction rate somewhat by reducing the external boundary layer, the mechanism believed to be primarily responsible for the larger increases is the cell disruption brought about by cavitation. Cavitation induced cell disruption and dispersion of suspended solids coupled with enhanced mass-transfer rates due to acoustic streaming are believed responsible for the increased mass-transfer rates. The solid-liquid extraction processes in which the application of acoustic waves results in increased extraction rates are:

1. Extraction of soluble matter from cellular solids (eg, sugar from sugar beets).
2. Solvent extraction (oils from oil seeds).
3. Extraction of alkaloids from herbaceous and plant-like materials.
4. Leaching of ores.

Table 1 summarizes some of the important extractions enhanced by ultrasound.

From the extensive amount of empirical data on extraction it can be concluded that both high and low-frequency acoustic waves enhance extraction rates. However, the intensity needed at lower frequencies to achieve the same degree of enhancement is smaller than that needed at higher frequencies. This suggests that cavitation (whose threshold is lower at low frequencies) with the accompanying cell destruction and mixing is the effective mechanism which promotes interphase mass transfer rather than microstreaming alone. It is apparent from Table 1 that ultrasonically-augmented extraction is particularly suited to the small-scale, batch type extractions needed in extraction of drugs from plants where minutes of ultrasonic ex-

Table 1. Summary of the important extractions enhanced by ultrasound

System	Frequency	Intensity	Comments
Extraction of sugar from sugar beets [13]	19.3 kHz		For the same yield the treatment with ultrasound reduces processing time from 60 to 45 minutes at 60–70°C and from 60 to 30 minutes at 50°C
Extraction of sugar from sugar beets [14]	100 kHz	800 W	Maximum increase in extraction (78%) was obtained by 45 minutes irradiation at 50°C
Extraction of sugar beets and sunflower seeds [15]	800 kHz, 1.9 MHz, 3.465 MHz	0.05 to 0.5 W cm^{-2}	An increase in yield of 12–14% for sugar beets and 27–28% for sunflower seeds was obtained. Some chemical change in materials was observed
Extraction of beer hops [16]	800 kHz	0.93 W cm^{-2}	At 13–18°C, an irradiation time of 3–4 hours resulted in a 62% saving in beer hops
Extraction of beer hops [17]	400 kHz	2 kW h	A saving of 30–40% in hops was achieved
Extraction of beer hops [18]	10–30 kHz	500 W	This is an example of an industrial unit treating 420 gal h^{-1} of liquid with over 50% savings in beer hops
Solvent extraction of coal with quinoline [19]	30–90 kHz	0.5 W cm^{-2}	The percentage made soluable is increased
Alcoholic extraction of oil seeds [20]	26 kHz	0–20 W cm^{-2}	830% increase in oil extraction rate with ultrasound
Extraction of peanut oil by hexane	400 kHz	6.5–62.3 W cm^{-2}	Extraction yield with ultrasound was increased by 2.76. Ultrasonic extraction is equivalent to using a mechanical stirrer at 1 200 rpm
Extraction of cassia acutifolia [22]	20 kHz		With 3 minutes of extraction with ultrasound the same amount of alkaloid was extracted as in 10 minutes of conventional extraction

traction can replace the Soxhlet process needing hours. However, Skauen [30] states that unless careful precautions are taken, over-irradiation by acoustic waves may lead to degredation of some of the extracted alkaloids. Mullard [31] and Brown [32] have reported that extraction equipment is being used in the perfume industry with an estimated pay-off time of less than a year.

Emulsification

Acoustic emulsification offers the following improvements over conventional methods (eg, rotating impellers, colloid mills and homogenizers):

1. The emulsion produced has particles in the submicrometre range with an extremely narrow particle size distribution. In our laboratory the mean particle size of an acoustic emulsion was found to be between 0.18–0.37 μm.
2. The emulsions are more stable.
3. Addition of a surfactant to produce and stabilize the emulsion is not necessary.
4. The energy needed to produce an emulsion by acoustic waves is less than that needed in conventional methods.

Industrially, acoustic emulsification has been used to produce a vegetable cocktail which is more stable than that produced with high-speed propeller mixers.[33] This industrial unit treats 25 gal min^{-1} of emulsion at a pressure of 250–300 psia with the ultrasonic energy being produced by a 15 hp motor to produce a well homogenized cocktail. In addition, ultrasonic homogenization is used routinely for industrial production of worcestershire sauce, cream type soups and peanut butter. Fig.1 shows a typical on-line homogenizing unit.

Schall [34] reports that a 10 hp motor can produce up to 1 000 gal h^{-1} of emulsion paint with better flocculation resistance, without foam production and with superior application and flow characteristics. Acoustic emulsification has also recently been used in mixing of test paper coatings,[35] in the continuous manufacture of wax sizing emulsions [36] and pigment dispersions.[37]

Gopal [38] states that a acoustic jet generator may require a 5–7 hp drive while working at 150–200 lb in^{-2} to process 1 000 gal h^{-1} of liquid giving 1 μm size particles, whereas a high-pressure homogenizer with similar performance will work at 1 000–5 000 lb in^{-2} with a 40–50 hp drive. Sonic homogenization therefore appears to be much more efficient than conventional techniques.

Recently there has been an interest in the use of oil-water emulsions to replace oil in order to produce a cleaner and more efficient fuel. Use of such fuel-water emulsions has been reported [39–41] in furnaces, cars and some postal

System	Frequency	Intensity	Comments
Extraction of alkaloid from datura stramonium [23]	20 kHz, 40 kHz		For 30 minutes maceration time yield was 9% higher with ultrasound. For longer periods the effect of ultrasound became less significant
Extraction of ravolfia serpentina roots [24]	25 kHz		Ultrasonic extraction reduced conventional extraction time from 8 hours to 15 minutes
Ipecac root [25]	20 kHz		1/2 minute extraction with ultrasonic horn produced extract greater than 5 hours of extraction with Soxlet extraction
Jaborandi leaves [26]	20 kHz		A 15 second irradiation extracts more alkaloid than 5 hours of Soxlet extractraction. After 15 seconds there is a rapid degradation of extract
Extraction of morphine from poppy plants [27]	500 kHz		15–17 minutes of ultrasonic extraction was equivalent to 24 hours of conventional extraction
Leaching of copper ores [27]	19.2 kHz	0.5 W cm^{-2}	Leaching at 25–45°C with ultrasound reduced the time necessary for mixing using a rotary mixer at 175–500 rpm from 20–60 minutes to 5–10 minutes with a 5–15% higher yield
Leaching of copper ores [28]	18.8 kHz	2.8 W cm^{-2}	Ultrasound increased leaching of copper 2–3 times
Leaching of zinc calcine [29]	22 kHz	4 W cm^{-2}	The leaching of Zn, Fe and Cu with H_2SO_4 solutions at 60°C was increased 0.1 to 102.7% with the improvement becoming smaller as the volume of slurry treated was increased

Fig.1 Typical on-line homogenizing unit (Sonic Engineering Corp)

service trucks with fuel economies of the order of 20% along with a reduction in air pollution. Other examples of acoustic homogenization on an industrial scale are in the cosmetic industry [42] and the pharmaceutical industry.[43]

A new and unusual example of the use of acoustic energy is in a recent application of ultrasonic emulsification involving the preparation of a stable polyster resin using 90 kHz ultrasound at an intensity of 40 kW gal^{-1}. Upon addition of a catalyst and a promoter this resin can be solidified to form a microporous object or sprayed as a coating.[44]

An excellent discussion of the fundamental principles of emulsion formation has been given recently by Gopal.[38] A discussion of the various mechanisms involved in acoustic emulsification is given by Fogler.[4]

Defoaming

The necessity of breaking foams arises often in many industrial operations as well as in sewage treatment plants.[45–50] The ultrasonic techniques used in breaking foams are mechanical and have the advantage that one does not have to add a chemical contaminant to break the foam. Most liquids with viscosities up to 500 cp can be acoustically defoamed. Although the exact mechanism of acoustic foam disintegration is not entirely understood, the following acoustic effects have been postulated by various authors to contribute to the disintegration process. (a) the partial vacuum on the foam bubble surface produced by the first-order acoustic pressure, (b) the impingement of the second-order radiation pressure on the bubble surface, and (c) the response of the foam bubbles to certain natural resonant frequencies which create interstitial friction causing bubble coalescence.

In addition to the mechanisms listed above, we have observed other phenomena which may prove considerably more important in foam breakage. (d) the instability of varicose waves in the foam film induced by acoustic waves (preliminary studies on single liquid films in our laboratory have clearly demonstrated the presence of this type of wave); (e) cavitation; (f) atomization was observed to occur from the film surface; and (g) the acoustically induced convective streaming currents we observed may produce high shear stresses which result in foam rupture

In suppressing the foaming of a jet aircraft fuel JP3 during rapid climb, a Hartmann type of air siren operating at 27.5 kHz and 145 dB was employed to break up 0.5–1 cm of very light fuel foam.[51] Dorsey [52] could control a foaming rate of 0–0.25 m^3 min^{-1} during fermentation operations using sirens working at 26, 29 and 34 kHz at about 145 dB. A device for defoaming corrosive liquids formed during preparation of photographic emulsions (for photographic gelatin silver halide emulsions) operating at a frequency of 10–100 kHz is reported in recent literature.[53] An apparatus for defoaming coating colour is described by Adams.[54] The use of air whistles in defoaming operations requires a minimum energy of 145–150 dB. They appear to be most efficient at frequencies below 15 kHz [55] (however, at these frequencies noise pollution would have to be controlled) and require air at a rate of 0.28 m^3 min^{-1} to break a foam at the rate of 0.028–0.56 m^3 min^{-1}. However, steam jet whistles have been reported to break foams [56] at rates of up to 0.31 m^3 min^{-1}.

Recently, the Sontrifuge defoamer has been developed by Rich [57–60] which incorporates centrifuging action to keep the foam concentrated in the centre of the basket to directly face the sonic beam (Fig.2). This sontrifuge has a liquid handling capacity of 10–500 gal min^{-1} at 260–440 revs min^{-1}. In summary, acoustic defoaming is a particularly viable alternative when the addition of a chemical defoaming agent will contaminate the liquid to be defoamed.

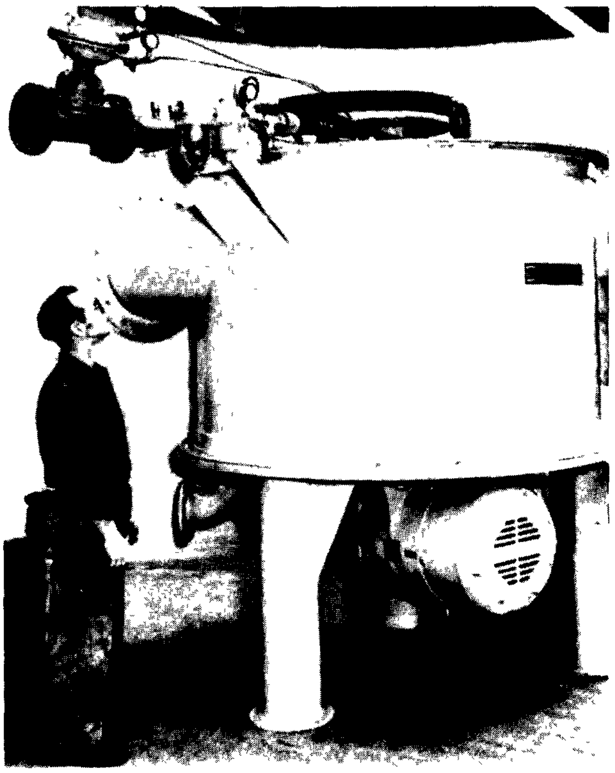

Fig.2 Large defoaming unit combining the effects of centrifugal force with ultrasound (Teknika Inc)

Waste treatment

Ultrasonic energy also finds applications in the field of industrial effluent and municipal sewage treatment plants. The acoustic energy acts primarily in two ways to aid the waste water treatment:

1. Clumps of bacteria and viruses are broken up along with suspended particles to form an emulsion.

2. When ozone is bubbled through the treatment chamber, ultrasonic waves keep the bubbles from coalescing and hence expose the maximum surface area to oxidation attack.

These two steps combine to give an improved water quality after the treatment.[61–63]

A pilot plant is in operation which processes 20 000 gal of sewage daily and in which 60 seconds of ultrasonic and ozone treatment has proved capable of destroying 100% of the fecal bacteria and viruses, 93% of the phosphates and 72% of nitrogen compounds.[64] A larger plant to treat 600 000 gal of sewage per day is scheduled to start in Indiantown, Florida. The ultrasonic ozone treatment may well replace the conventional chlorine treatment of waste waters.

Chemical reactions

Application of ultrasound to mass transfer limited chemical reactions can enhance the overall reaction rate. This is particularly evident in gas-liquid reactions or heterogeneously catalysed reactions. For example, the use of acoustic energy in a continuous stirred tank reactor in which methylmethacrylate was being polymerized resulted in a rapid increase in conversion and a smaller increase in degree of polymerization.[65] Another example of increased reaction rates due to facilitated interphase mass transfer is gas-liquid polymerization. Kokorev et al [66] described a gas-liquid reactor having an intense acoustic field for the continuous production of polycarbonates by interphase polycondensation of an aromatic dihydroxy compound with phosgene in the presence of CH_2Cl_2. In the presence of ultrasound, the di-hodroxy compound solution formed a highly-dispersed emulsion with CH_2Cl_2. When phosgene was bubbled through the emulsion a 94% yield of polycarbonate was obtained in 25 seconds for the acoustically-formed emulsion. This compares with 3 600 seconds required for a stirred reactor working at 4 200 rpm.

The exposure of cotton seed delint to ultrasound of 1 MHz during hydrolysis in 36–41 % HCl resulted in a 1.2–2 fold increase in the hydrolysis rate.[67] Application of ultrasound to heterogeneous catalytic systems can also result, in some cases, in greatly increased reaction rates. Application of ultrasound in the hydrogenation of olive oil with Raney nickel catalyst, for instance, resulted in a noticeable acceleration of the reaction rates but with reduced selectivity.[68] Thus, when 1 MHz ultrasound was applied at intensities of 0.6, 1.8, 2.4, and 3.0 W cm^{-2} the iodine number of the hydrogenated sample after 3 hours was 77 without ultrasound, 70 at 0.6 W cm^{-2}, 56.4 at 1.8 W cm^{-2}, 34.2 at 2.4 W cm^{-2} and 50.0 at 3.0 W cm^{-2}. Other examples of the facilitation of heterogeneous reaction rates with acoustic energy are the sonochemical oxidation of phenol in acqueous solution [69] and the manufacture of supported catalysts.[70, 71] A review of the effect of ultrasonic waves on heterogeneous catalysts is given by Parypczak.[72]

Heat transfer

Microstreaming and cavitation which lead to increased mass transfer rates, will also facilitate heat transfer processes. The effect of acoustic energy on three different heat transfer mechanisms will be considered, viz: (a) acoustic drying of fine particles and cellular material, (b) crystallization and (c) boiling heat transfer.

Drying

Acoustic drying is of great potential importance in the treatment of thermolabile materials such as those in the food and drug industries. This method of drying increases the rate of moisture removal, decreases the final moisture content and has the advantage over high velocity gas drying that the material is not blown away or damaged. Soloff used a rotary drier with a sonic source of 169 dB at 10.9 kHz on a pilot plant scale to study the enhancement of drying rates of different substances.[73] Table 2 summarizes his results. In addition to the considerable enhancement of drying rates, the heat sensitive substances (eg, ascorbic acid) were not degraded in any form. Fairbanks [74] reports a similar 10–40% increase in drying rate of 100 mesh coal in a rotary drier with sound of 150 dB at 12–20 kHz compared to the no sound case. Sugar crystals exposed to 50–30 000 Hz sound at 130 dB are dried to a moisture content which is 1/4–1/2 of that obtained in equivalent time for drying without acoustic assistance.[75]

Crystallization

In crystallization operations the heat transfer rate drops because of incrustation on the cooling coil. Sonic vibrations can be effectively used to prevent scale formations on the heat transfer surface. Fedotken et al [76] reports that the installation of four ultrasonic generators of 21 kHz, 1–5 kW at the bottom of a sugar juice concentrator reduced sugar accumulation at the bottom by 80%. It has recently been demonstrated that application of 20 kHz ultrasonic vibration to a stainless steel coil (Fig.3) results in a marked improvement in preventing scale deposition and hence faster rate of crystallization.[77] A British patent describes the application of sonic vibration at 13 kHz to prevent the icing of the cooling coil and claims a maximum heat flux of 450 kcal ft^{-2} h^{-1} was possible with sonic vibrations, whereas

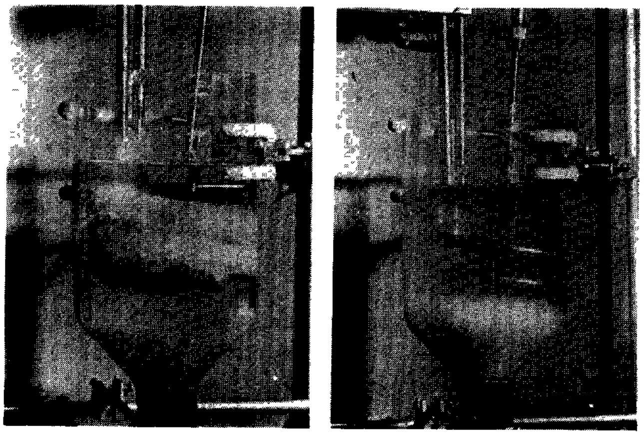

Fig.3 Crystallization of potassium nitrate from a 28% aqueous solution left – crystallization has ceased because of crusting on the coil, right – crystallization is proceeding with incrustation prevented by ultrasonic vibration of the stainless steel coil

Table 2. Summary of Soloff's results using a rotary drier with a sonic source of 169 dB at 10.9 kHz on a pilot scale to study the enhancement of drying rates of different substances [73]

Material	Initial moisture [%]	Desired final moisture [%]	Retention time read [min]	Sonics feed rate [lb h^{-1}]	No sonics feed rate [lb h^{-1}]	Increase in throughput due to sonics [%]
Wood flour	5.5	1.53	3.0	90	37	143.2
Orange crystals	3.5	1.8	15.0	38	8	375.0
Grated cheese	16.8	5.9	16.2	35	25	40.0
Powdered coal	19.2	2.0	5.0	110	48	129.2
Antacid powder	15.1	6.0	15.0	27	15	80.0
Gelatin beads	12.9	3.7	20.0	22	12	83.3
Enzyme crystals	9.8	6.4	120.0	5	2	150.0
Rubber crumb	44.0	6.0	90.0	7	4	75.0
Carbon black pellets	48.7	1.0	25.0	18	12	50.0
Polystyrene powder	0.5	0.1	30.0	14	6	133.3
Aluminium oxide	0.5	0.2	5.0	56	32	75.0
Metallic soap of fatty acid	27.0	0.4	60.0	10	4	150.0
Rice grains	27.6	14.5	11.0	40	18	122.2

in the absence of sonic [78] vibrations the maximum heat flux possible was 90 kcal ft^{-2} h^{-1}.

The application of ultrasound in the crystallization process is a most effective method for the preparation of a fine crystallization product that is homogeneous with respect to grain size.[79–81] Crystal clevage resulting from cavitation and the suspension of fine particles due to the stirring action of ultrasonic waves results in a uniform crystal growth rate and a product whose size distribution is uniform.

Boiling heat transfer

Ultrasonic cavitation resulting in bubble turbulence increases the heat transfer rates in nucleate boiling.[82,83] A possible application is in the operation of distillation columns.

Miscellaneous applications

Sonic and ultrasonic devices are also being used for treatment of fibre filaments,[84] in pulp refining and pigment dispersion,[85] for air pollution control, control of impregnation of paper and boards,[86] in preparation of emulsions, sizing dispersions and acceleration of dyeing in the textile industry,[87] sterilization of heat sensitive materials like plastic syringes,[88] in sonic distillation,[89] liquid atomization [90] and aerosol coagulation.[91]

Conclusion

The areas of industrial application of acoustic energy in new processes or to speed up existing ones are many and varied. Table 3 gives an estimated sales volume for ultrasonic equipment.[92] With the development of higher intensity units, continuous flow units and focusing devices, ultrasound will continue to be used even more extensively. A large body of literature exists on promising results on the laboratory scale. Design and development work needs to be done to use these results to process the large turnover needed in the chemical processing industry

Table 3. Estimated sales volume of ultrasonic equipment (millions of US dollars)

Use	1968	1973
Cleaning	18.0	30.0
Instrumentation	15.0	30.0
Medical	7.0	30.0
Miscellaneous processes	7.0	22.0
Assembly	5.0	20.0
Electronics	5.0	10.0
Consumer products	0.1	10.0
Packaging	0.2	5.0
Textiles	0.1	5.0
Total	74	162

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