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ULTRASONIC EMULSIFICATION OF PETKOLIN

Part I. Pure Petkolin in Water and Petkolin–Kerosine Solution in Water System

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Abstract. A solution of Petkolin, a chlorinated pesticide, and kerosene with 27–33% (by volume) Petkolin content, has been emulsified in the matrix of water in the ratio of 1:6 to 1:10 (by volume) P–K/W mixture by treatment with ultrasonic radiation of 300–500 kc frequency range and 30–40 watts power range. The required radiation time was about 5–10 min which decreased to almost half on addition of 1% Teepol (by volume) of P–K/W mixture.

Petkolin (a chlorinated pesticide developed from the indigenous raw materials in the Chemical Engineering Section of PCSIR Laboratories Karachi) is used as pesticide in the form of P/W (Petkolin/water) emulsion on agricultural crops.

The emulsion is a thermodynamically unstable mechanical mixture of liquids that are immiscible under ordinary conditions.[1] One of them is dispersed in the other in the form of fine droplets at the expense of external energy supplied by the emulsator (the required amount of energy of emulsification is contained in the system as potential energy). There are, in general, two ways in which emulsification can be made to take place, namely, emulsification with chemical emulsifying agents, such as surface active materials, naturally occurring materials and finely divided solids and the emulsator or mechanical devices, e.g. simple mixers, colloid mills and ultrasonic homogenizer. The use of mechanical devices for mixing and shearing represents a simple way of introducing the required energy of formation of an emulsion. The usability of ultrasonic homogenizer for the production of emulsions is described by Harvey[2] Witkowski and Otowski and others.[4] When the ultrasonics of correct pressure travels through the liquids, it produces compressions and rarefactions that disrupt the media physically. Many small bubbles are apparently being produced within the liquid column and collapsing. This production and collapse, known as 'cavitation'[5,6] causes the emulsification.

The chemical emulsifying agent used to produce P/W emulsion is imported. The ultrasonic emulsification is, therefore, tried. It is found that 27–33% (by volume, depending on Petkolin density) of Petkolin–kerosine solutions in 1:6 to 1:10 (volume ratio) water yielded emulsion when treated with ultrasonic radiation of 300 and 500 kc/s frequencies and 30–40 watts energy for 5–10 min.

Experimental

Ultrasonics generator of Schoeller & Co., Germany, was used. This set is designed to use removable piezoelectric transducers of the frequency range of between 300 kc/s and 2 mc/s with the output power from 18 to 420 watts. The radiating area of the surface transducers is a concentric circular surface of 6.2 cm dia and can be operated up to 90°C. The block diagram of the Ultrasonic Laboratory set is shown in Fig. 1. The tuned power output in watt against the power adjustment switch positions for different transducers are plotted in Fig. 2. The frequency of the high frequency generator is tuned to the mechanical fundamental frequency of the respective sound transducer with the help of a tuning condenser. In the tuned condition the output power

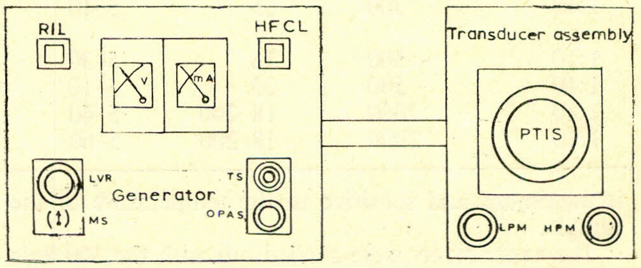

Fig. 1. Block diagram of ultrasonic laboratory set RIL–Ready Indicator Lamp; HFCL–High Frequency Control Lamp; LVR–Line Voltage Regulator; MS–Main Switch; TS–Tuning Switch; OPAS–Output Power Adjusting Switch; PTIS–Piezoelectric Transducer and Irradiating Surface; LPM–Low Pressure Manometer; HPM–High Pressure Manometer.

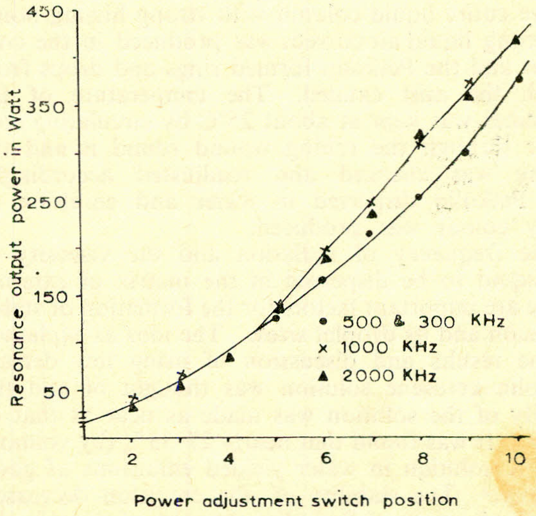

Fig. 2. The plot of radiation energy in watt against power adjustment switch position for transducers of different frequencies.

TABLE 1. EMULSIFICATION OF PURE PETKOLIN.

Petkolin conc (% by volume)	Frequency of radiation (kc/s)	Power output (watt)	Time of irradiation (min)	Emulsion formation	Remarks
5	300	18	60	Nil	
,,	,,	35	,,	,,	
,,	,,	60	,,	,,	
,,	,,	85	,,	Slight	Unstable
,,	,,	100 and above	,,	Full	Unstable complete downward sedimentation in a day or so.
,,	500	>100		,,	,, ,, ,, ,, ,,
,,	1000	,,	,,	Nil	
,,	2000	,,	,,	,,	

TABLE 2. EMULSIFICATION OF 27–33% PETKOLIN–KEROSENE SOLUTION IN WATER.

Ratio of Petkolin–kerosene solution with water	Frequency of radiation (kc/s)	Power output (watt)	Time of irradiation (min)	Emulsion formation	Remarks
1:10	300	18	5–30	Partial	Emulsification incomplete due to low output. Emulsion stable; slight upward creaming after a month.
1:10	300	35	5–10	Complete	Stable; slight upward creaming after a month.
1:10	500	18	5–30	Partial	Ash with 300 kc/s.
1:10	500	35	5–10	Complete	,, ,,
1:10	1000	18–200	5–60	Nil	Two phases remained separated and distinct.
1:10	2000	18–200	5–60	Nil	

is maximum and sensitive to the temperature of the sample.

The experiments were carried out with the 300 kc/s and 500 kc/s transducers to emulsify 5% (by volume) pure Petkolin in water. The viscous Petkolin fell to the bottom of the container and failed to form emulsion at low energy (40 watt or less, see Table 1). With the increase of output energy (~125 watt) the ultrasonic action was accompanied by violent stirring of the entire liquid column with strong hissing noise. A strong liquid air current was produced in the container and the Petkolin formed rings and drops from which the mist exuded. The temperature of the container was kept at about 25°C by circulating cold water through the tubing wound round it and the tuning was checked and readjusted accordingly. The Petkolin dispersed in water and emulsion of milky colour was produced.

The frequency of radiation and the viscosity of the liquid to be dispersed in the matrix of external phase are important factors for the formation of stable emulsion and its droplet sizes. The idea as explained in the results and discussion of using low density Petkolin–kerosene solution was thought of and the density of the solution was made as near as that of water. It was found that nearly 27–33% (by volume) of P–K solution in water yielded emulsions of good stability.[2] The stability of the emulsion decreased with the increase of Petkolin concentration as in the case of oleic acid.[7] The appropriate percentage of P-K/W mixture for emulsification were determined by performing a series of experiments.

Results and Discussion

Pure Petkolin in water emulsions (Table 1) formed with high energy ultrasonics were unstable and complete 'downward creaming,[1] was taking place in a day or so.

According to Stokes[8] the sedimentation rate u of the spherical droplet of radius r and density d_1 in the medium of liquid of viscosity η and density d_2 is given by

$$u = \frac{2gr^2\,(d_1 - d_2)}{9\,\eta}$$

Where g is the acceleration of gravity. The sign of u and hence the direction and rate of movement of the

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Suppose equal volumes of two liquids, liquid 1 and liquid 2 of densities d_1 and d_2 respectively, where $d_1 > d_2$, are to be emulsified at the expense of mechanical energy E in the matrix of another liquid. Intermolecular force F_1 of liquid 1 is greater than that of liquid 2, i.e. $F_1 > F_2$, due to the fact that intermolecular space S_1 of liquid 1 is less than S_2 of liquid 2, i.e. $S_1 < S_2$.

Now, the amount of energy E spent to form, say, X droplets of liquid 1 which is contained in the system as potential energy will produce $X+Y$ droplets of liquid 2. Since the energy of formation of droplet of liquid 1 is greater than that of liquid 2, i.e. in order to equate the energy E the liquid 2 will be divided into more droplets. From the above considerations, the droplet radius r_1 of liquid 1 is greater than that of liquid 2, i.e. $r_1 > r_2$.

droplets depend on the relative values of densities. In P/W emulsions, the density d_1 of Petkolin is greater, and therefore, 'downward creaming' or sedimentation was taking place. Examination of the above equation leads to the conclusion that instability of P/W emulsion was probably due to the large droplet radius and greater density difference between the disperse and continuous phases.

As mentioned before 27–33% of P–K solution was taken, in place of pure Petkolin to make the value of d_1 of the disperse phase very nearly equal to d^2 of continuous phase and thereby improve the stability of the emulsions.

The height of the liquid column above the transducer is an important factor in the technique of ultrasonic emulsification. It was found that to keep the time and energy for producing emulsions as recorded in the Tables 1 and 2, the liquid column should not be more than 8 cm high. It was necessary to increase the time and energy with the increase of the height of the column and above 20 cm emulsions could not be produced even by doubling the parameters.

As shown in the Table 2 the range of frequency for yielding P/W emulsion was experimentally found to be from 300 to 500 kc/s, the suitable energy of radiation for the production of 1:6 to 1:10 (volume) of P–K/W emulsion, forming 6–8 cm of liquid column above the transducer in 3–10 min was in the range of 30–40 watt. The emulsions produced as above were of much improved stability and showed slight upward or downward creaming after a month or so. The time of emulsification was greatly reduced on the addition of 1% (by volume of P–K/W mixture) of Teepol. Quantities of Teepol above 1% did not help to reduce the emulsification time or its stability but floated on the surface as white soapy-foam. The pesticidal activities of the emulsions produced as in Tables 1 and 2 were tested on laboratory scale; the authors believe that due to fine droplet sizes of Petkolin–kerosene mixture in the emulsions they may have more efficient pesticidal activities. The experiment was repeated with 1000 and 2000 kc/s radiations of high and low energies. It was found that even after 7 hr of irradiation it was not possible to produce P/W or P–K/W emulsions.

The details of the method such as applied energy of radiation against time of emulsification, energy against quantity of P–K/W mixture and the droplet sizes are under careful study.

It is suggested that the emulsions in industrial scale can be produced with the help of a specially designed ultrasonic unit having transducer fitted at an angle on one end of a channel so that the radiation can be reflected a number of times from reflectors mounted on the side walls in the length through which P–K/W mixture is made to flow in such a rate that the emulsification is completed during the transit.

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